CROSSLINKED POLYMER GEL SYSTEMS DEVELOPMENT FOR WATER SHUT-OFF JOBS IN HYDROCARBON RESERVOIRS

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THESIS

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It is certified that the work contained in the thesis titled **“Crosslinked Polymer Gel Systems Development for Water Shut-off Jobs in Hydrocarbon Reservoirs”** by **REENA** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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Dedicated

to my

Beloved Parents

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SYMBOLS

ATR : Attenuated total reflectance

cc : Cubic centimetre

cm : Centimetre

cm^{-1} : Reciprocal wavelength

cP : Centipoise

CR : Controlled rate mode

DSC : Differential scanning calorimetry

D_p : Particle diameter before gel treatment

ΔD_p : Particle diameter after gel treatment

Δ : Change of a value

EOR : Enhanced oil recovery

F_{rro} : Residual resistance factor for oil

F_{rrw} : Residual resistance factor for water

FESEM : Field emission scanning electron microscopy

FTIR : Fourier transform infrared spectroscopy

gm : Gram

g/mm^3 : Gram per millimetre cube

G’ : Elastic modulus

G” : Loss modulus

Hz : Hertz (cycle per second)

IOR : Improved oil recovery

mL : Milliliter

mm : Millimeter

mm/s : Millimeter per second

M_w : Wet weight of the polymer

M_d : Dry weight of the polymer

nm : Nanometre

NPs : Nanoparticles

OOIP : Original oil in place

ΔP_i : Pressure before gel treatment

ΔP_f : Pressure after gel treatment

P_b : Bulk densities of core particles

P_m : Medium densities of core particles

Pa : Pascal

Pa.s : Pascal second

PAM : Polyacrylamide

PNPs : Polymer coated nanoparticles

PPG : Pre-formed particle gels

PPR : Percentage permeability reduction

PSPMGs : pH-sensitive polymer microgels

PAtBA : Polyacrylamide or polyacrylamide tert-butyl acrylate

PV : Pore Volume

PVA : Polyvinyl alcohol

PVP : Polyvinylpyrrolidone

Rad/s : Radian per unit second

RF : Resorcinol formaldehyde

RPM : Rotation per minute

RRF : Residual resistance factor

s : Second

S_{oi} : Initial oil saturation

S_{or} : Residual oil saturation

S_{wi} : Initial water saturation

Temp. : Temperature

TSMGs : Temperature sensitive microgels

TGA : Thermogravimetric analysis

V_s : Flow velocity of brine

W_b : Fraction of bound water

W_f : Fraction of free water

Wt : Weight

w/v : Weight per unit volume

ZnO : Zinc oxide

Φ : Particle sphericity

ϵ : Porosity or void space before gel treatment

$\Delta\epsilon$: Porosity or void space after gel treatment

ω : Angular frequency

μ : Viscosity of brine

% : Percentage

ρ : Density of brine

λ_{wi} : Water mobility ratio before gel treatment

λ_{wa} : Water mobility ratio after gel treatment

PREFACE

Heterogeneity within the oil well causes the flow of injected fluid not to be uniform within the reservoir. It may consequence in very underprivileged sweep efficiency and accordingly, very high water to oil ratio in producing hydrocarbon reservoirs. Several reservoirs have practiced water flooding for extensive times subsequently their premature phases of progress. Due to the long time use of injected fluid, erosion takes place. It also helps in reservoir heterogeneity. Heterogeneity leads to water breakthrough within the producing wells along the high permeable zones or ruptures, then reduces oil production. To overcome excessive water problem and heterogeneity, the chemical methods including injection of gelling systems, preformed particle gels, in-situ gels, foams, etc. have been widely used for water control in hydrocarbon bearing reservoirs globally. In recent decades, excess water control or profile control was proposed to improve the efficiency of unswept zones, which has shown a clear effect on oil recovery. Among chemical methods, application of gels prepared using polymers and crosslinkers have been demonstrated to be a cost-effective technique and usually applied for enhancing oil recovery factor by controlling excessive water in reservoirs. Additionally, enhancement in the polymeric gel properties has been achieved with the use of nanoparticles within the hydrogel network. Presently, nanoparticles have presented favorable and good effects in resolving many issues of the oil and gas industry. Recently, nanotechnology has shown improved consequences in high permeable oil reservoirs for improving oil recovery. There are several nanoparticles ($Zr(OH)_4$, SiO_2, SnO_2, Al_2O_3, etc.), which are reported, have been widely used in the enhancement of oil recovery.

In this study, the first step was to identify and select suitable polymer and crosslinker for preparing gel. For the purpose, polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) polymers were used as polymer and resorcinol-formaldehyde (RF) as a crosslinker. Further laboratory synthesized *Moringa oleifera* leaf extract and ZnO containing green nanoparticles were also used in preparing gel. The research was then conducted to determine the effect of various parameters such as polymer, crosslinker and nanoparticle concentrations, salt, temperature, etc. on PVP:RF, PVP/PVA:RF, PVA:RF and PVP-ZnO:RF gel systems and on gelation time, gel strength, storage and loss modulus.

A spectroscopic tool, Infrared spectroscopy (IR) analysis was conducted to confirm the hydrogen bonding of the gel systems. Field emission scanning electron microscopy (FESEM) was used for further observations of the microstructure of gels. The thermal stability of gels was checked using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). To test the effectiveness related to sweep efficiency and water shut-off of gel systems, the sandpack/core flooding experiment was conducted at a high temperature of 90°C. This experiment showed a favorable reduction in permeability for all the gel systems. Ergun equation result exhibited that the diameter of core particles was increased by 10% after using polymeric gel systems.

Objective

The main objectives of this research work are:

- Identification of suitable polymers, crosslinkers and nanoparticles for preparing gels.
- Development of some blend, conventional and nanocomposite hydrogels using different polymers, nanoparticles and crosslinkers.
- FESEM and FTIR analysis of these newly developed gel systems to confirm new bond formations and morphological properties.
- Study of the thermal and rheological properties using TGA, DSC and rheometer.
- Study of the effect of the different polymer, crosslinker, salt’s concentration and temperature.
- Study the variation in rheological properties of developed conventional and nanocomposite hydrogels.
- To test the effectiveness of the developed gel systems to minimize excessive water production in hydrocarbon reservoirs.

Thesis Overview

In this research work, conventional and nanocomposite both types of gel systems were prepared. Polymeric gels, blend gels and nanocomposite gels were prepared using polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP) and resorcinol formaldehyde (RF). PVA and PVP were used as polymer, however, RF as a crosslinker. The pH of the gel systems was adjusted approximately 9 to increase the gelation time.

To overcome the confines of conventional gels (polymeric and blend gels), nanocomposite gels were prepared. These developed gel systems were thoroughly evaluated by various techniques.

The thesis consists of eight chapters, which are as follows:

Chapter 1

The first chapter of the thesis is a general introduction. In this chapter, different types of water production within the reservoirs have been discussed. Problems related to excess water and their treatment difficulty are also mentioned. Techniques, different types of polymers and crosslinkers used for water shut-off treatments and their factors affecting are described. In the end, the highlights of the chapter are concluded.

Chapter 2

In chapter two, a literature review of various gel systems used for excessive water control has been given. A literature review of enhanced oil recovery (EOR) is also described. Different gel polymer technologies including nanotechnology used by the hydrocarbon industry worldwide are also given. An insight into the preparation of gel systems for the water shut-off job is described here. The outlines and objectives of the present research work are also included in this chapter.

Chapter 3

This chapter of the thesis consists of the synthesis and characterization of the conventional and nanocomposite hydrogels to enhance oil recovery factor from hydrocarbon reservoirs. Synthesized gels were further characterized by using various analytical techniques like UV-Vis, XRD, FESEM, FTIR, etc. Different technologies used to characterize the developed gel system are also explained in this chapter.

Chapter 4

This chapter deals with bulk gelation study of prepared gels. Gelant solutions of different concentrations were prepared and placed in scintillation vials. After that, scintillation vails were placed in the preheated oven at various desired temperatures. The gelation time was recorded by visual observation of vials and viscosity determination of the gelants at certain time intervals. Gel strength was measured using a breakthrough vacuum method. The main objective of the bulk study was to investigate the effect of polymer, crosslinker concentration, temperature, pH and salinity on gel strength and gelation time. These are included in the present chapter.

Chapter 5

Reaction mechanism, ultraviolet-visible (UV-Vis), x-ray diffraction (XRD), FTIR spectra of developed gel systems are discussed in this chapter. Morphological (FESEM) study along with energy-dispersive x-ray spectroscopy (EDS) of these gel systems has also been described and included in the chapter.

Chapter 6

In this chapter, the thermal and rheological study of conventional and nanocomposite gels has been given. Thermal and rheological properties of developed gels change when polymer or crosslinker or nanoparticle concentration varies. Conclusions obtained from these studies are well explained in this chapter.

Chapter 7

Core/sandpack flooding and Ergun equation results are discussed in this chapter. The objective of this study is to evaluate the effectiveness of polymeric gel systems in the sandpack/core. Pre and post gelation permeability was determined. The residual resistance factor (RRF) and percentage permeability reduction (PPR) was calculated to determine the reduction in permeability. Change in particle diameter was measured using the Ergun equation.

Chapter 8

This chapter mainly consists of the summary and conclusions of the thesis work based on the thorough studies of the gels.

CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

Increasing demand for fuel and other petroleum products has forced the petroleum industry to exploit the newer as well as existing petroleum wells as much as possible. A newly discovered oil well has a natural drive to push the crude oil from deep down the surface to the top of the well which is termed as primary recovery. After this, an external drive is required to recover the oil from well exhausted of natural drive generally achieved with the help of pumps, which is called the secondary recovery of oil. After a certain stage (40-50% recovery of oil) producing the oil from a well with the help of pumps becomes uneconomical due to high pumping costs and other factors that make it highly difficult for pumps to recover the oil. Then, we need some chemical or physical treatment of the well, which results in the further economical production of oil that is termed as the tertiary or enhanced oil recovery (EOR).

The traditional primary recovery method can recover one-third of the original oil in place (OOIP); this method depends on the hydrocarbon and reservoir drive. Secondary recovery is generally water flooding, it recuperates 20-50% of the original oil in place (Gbadamosi et al., 2019). EOR is generally suggested after the secondary recovery. As a significance, EOR methods have grown attention from the research and development phases to the oilfield implementation stage. This interest has been also expanded by current high oil prices, maturation of oilfield and uncertainty about the future oil supply (Difiglio, 2014). EOR processes are generally applied in the case of heavy viscous oils and oilfields with no primary and secondary productivity (Du et al., 2013). The efficiency of the EOR methods greatly depends on the reservoir characteristics and the nature of the displacing and displaced fluid (Pal et al., 2018). These reservoir characteristics include petrophysical properties like capillary pressure, relative permeability, wettability of the rock and degree of reservoir heterogeneity, etc. (Falode and Manuel, 2014; Habibi et al., 2019). In order to reduce the negative effect of some of these reservoir properties like relative permeability, surface and interfacial tension of the reservoir fluids, some new polymer flooding methods are available to reduce water production (Alfazazi et al., 2019; Mishra et al., 2014). These polymers reacted with the porous media of the reservoir and formed thick adsorbed layers to minimizing water production and maximizing oil production (Aramideh et al., 2019).

Oil production was introduced in the year 1950 as a major industrial activity worldwide, which is one of the most essential energy resources until now. During oil production, it was observed that after secondary recovery, oil production reduces and excess water production increases, which leads to corrosion, high disposal costs, negative environmental effects, etc. (Bailey et al., 2000; Yortsos et al., 1999; Holanda et al., 2018). Excess water production is a major problem in the oil industry. Produced water is a serious concern in maturing oil reservoirs that leads to some additional reservoir issues such as scale formation, emulsion bacteria and corrosion problems, which may arise because of the high water cut. Globally, the oil industries spend billions of US dollars every year to address the problem of excess water production (El-Karsani et al., 2015). Problems generated from excess water production can be categorized into two main categories: The first category (production of excessive water in production wells) is produced by the flow of fluid from a high permeable zone because of the heterogeneity of the reservoir. It leads to minimum oil production due to viscous fingering in the reservoir. The second category (leakage of water) mainly is because of casing leaks, water channeling behind pipes and water coning through the matrix. These all are the main reasons for the production of excess water (Hatzignatiou et al., 2016; Mohamed et al., 2018).

Due to excess water production, a lot of oil stays in the low permeable zones, because excess water flows from high permeable zones. Produced excess water not only hinders oil recovery but also significantly reduces the profitability of production (Chen et al., 2015; Seright et al., 2003; Sydansk and Seright, 2006). Water production along with oil production is one of the major concerns of the oil industries. Excess water reduces well productivity of the industries (Johnston et al., 2019). Excess water production has a negative impact on oil recovery, it consists of loss of profits as oil production decreases. Handling cost and other expenses related to treatment and disposal of excess water are very high (Kumar and Mandal, 2017). It is expected that an average of three barrels of water is produced to each barrel of oil during oil production, worldwide (with the ratio at 7:1 in United states and 55.5:1 in the North Sea) (Bailey et al., 2000; Halliburton report, 2013; Mohammadi, 2018). The total cost of treatment, disposal and separation of excess produced water has been estimated to be about 50 billion dollars annually in the oil industry (Halliburton report, 2013).

There are various thermal and non-thermal techniques which are used to reduce excess water production. These methods not only shut-off or slow down water production, but also considerably increases oil production and extend the life of the reservoir (Hill et al., 2012). It is estimated that about 210 million barrels of water are produced daily supplemented with 75 million barrels of oil production worldwide (Mohammadi, 2018).

Jackson and Myers, (2003) estimated the average cost of disposal methods for the produced water as presented in **Table 1.1** given below.

Table 1.1 Disposal cost of produced water

Sl. No.	Method	Estimated cost (dollar/billion)
1	Surface discharge	0.01-0.80
2	Secondary recovery	0.05-1.25
3	Shallow re-injection	0.10-1.33
4	Evaporation pits	0.01-0.80
5	Commercial water hauling	0.01-5.50
6	Disposal wells	0.05-2.65
7	Freeze thaw evaporation (FTE)	2.65-5.00
8	Evaporation pits + flowlines	1.00-1.75
9	Constructed wetland	0.001-2.00
10	Electro-dialysis	0.02-0.64
11	Induced air flotation for de-oiling	0.05
12	Anoxic/Aerobic granular activated carbon	0.083

1.1 Types of Water Production

Produced excess water during oil recovery is responsible for the early maturation of the reservoirs. Produced water can be divided into following three different categories as good, bad and sweep water (Bailey et al., 2000):

1.1.1 Good Water

Good water production takes place normally due to altering flow lines from the injector to the producer well. Water breakthrough occurs into high permeable zones, while oil is still being swept into many other low permeable zones. This produced water is extracted along with oil and gas production most of which is inoculated underground, either to enhance oil recovery or easily disposable (Al-Muntasheri et al., 2007; Nasiri et al., 2017; Wu et al., 2006).

1.1.2 Bad Water

Bad water is the excess water produced from the wellbore during petroleum production. This water is responsible for the reduction in oil production. The cost of disposal of bad water is also very high. This bad water can cause corrosion, casing, packer leaks or tubing. Bad water is also the reason for channeling behind the casing. This produced bad water is much more than the economic limit of water to oil ratio and its management is also not easy. Worldwide, the disposal cost of this bad water is 50 billion dollars (Halliburton report, 2013).

1.1.3 Sweep Water

Sweep water comes from either an active aquifer or an injection well. Management of this sweep water is very essential and it affects the major part of the reservoir. All reservoirs either from water flood or natural aquifer produce excess water during oil recovery. This co-production of sweep water leads to the early stage maturity of the reservoir (Nriagu et al., 2017).

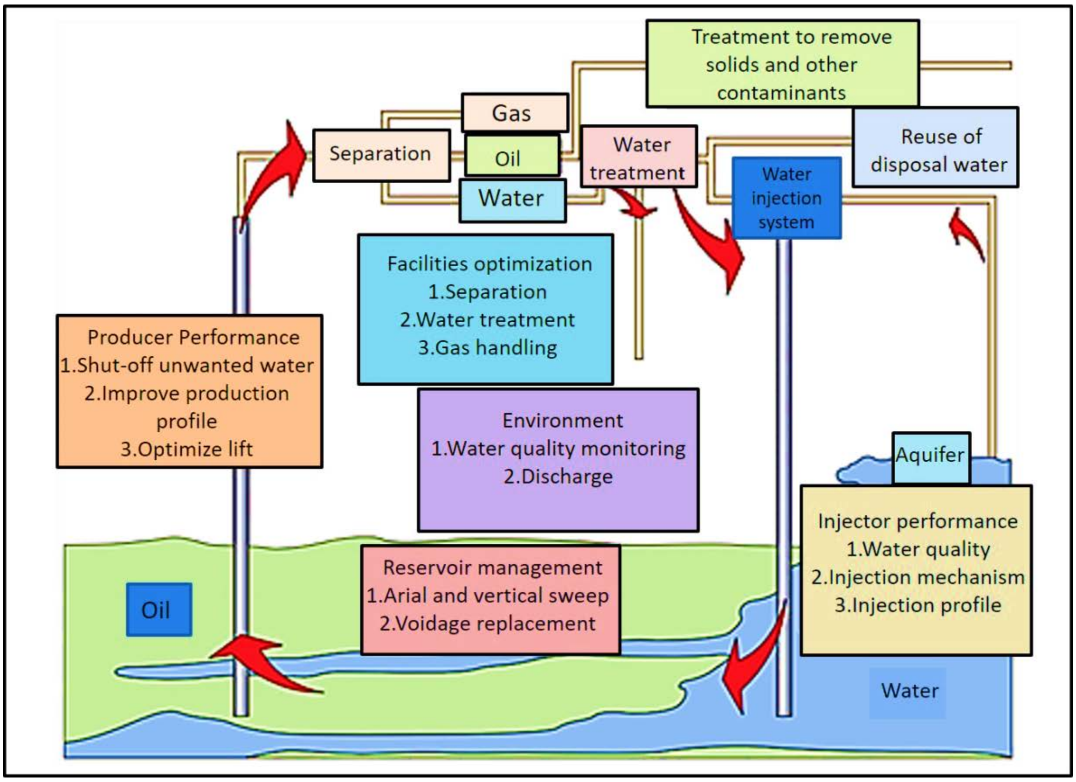

Figure 1.1 Produced water management in oil and gas reservoirs (Arnold et al., 2004).

Inadequate management of produced water before its discharge is found to be harmful to the environment. Treated water again can be used as displacing fluid. Regulations regarding disposal of this produced water are also getting stricter, disposal options are also very limited. Water management in oil and gas reservoirs is shown in **Figure 1.1** (Arnold et al., 2004; Smith et al., 2017).

Oil productivity from oil wells can be increased by reducing excess water production from the reservoirs. Many chemical and mechanical methods have been developed to control excess water and to minimize the effects, which produce due to excess water. Before using any chemical or mechanical method, the water problem should be diagnosed properly (Alomari et al., 2013; Brice et al., 2014; Bybee, 2011). The techniques to minimize excess water control can be divided into two groups.

These are excess water control and disposal techniques. It is well-known that produced water contains many serious contaminants. This water also contains some natural bodies such as microorganisms, these can have a negative impact on the environment. In many developing countries, contaminated water is a severe cause of thousands of deaths per day due to the toxification of consumable water and unfiltered sewage. Without any proper treatment, this produced water is discharged into sewage. Therefore, it is necessary that disposal techniques have to put on the standard strategies to minimize negative environmental impacts. But the disposal of produced water, according to standard guidelines, increases the discharging cost from 30-40 billion dollars globally (Ariaratnam et al., 2015).

1.2 Problems Related to Water Control

Water control problems can be classified into one of two major categories:

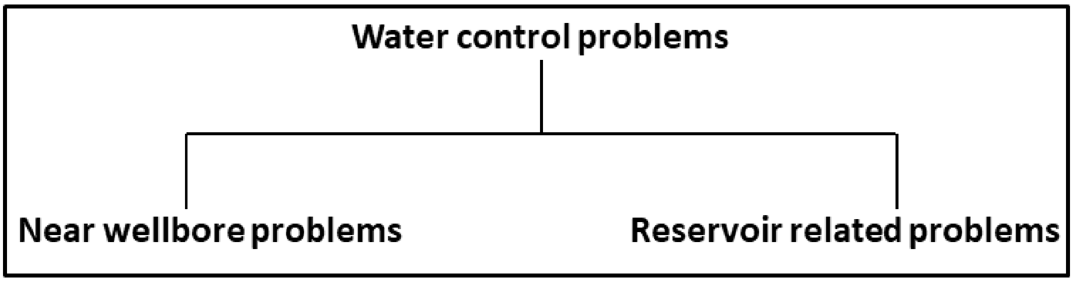

Figure 1.2 Types of water problems.

1.2.1 Problems Related to Near Wellbore

Mechanical and chemical are two main near wellbore problems. The production of oil and gas from an oil well involves chemical and mechanical methods, which have a negative impact on the wellbore. Many of these methods can eventually cause a problem with the well, resulting in either the failure of equipment or a decrease in oil production. Mechanical problems are due to casing (hole in the wellbore due to corrosion, perversion of formation or high pressure), poor mechanical integrity of the packers. Wellbore leakage occurs in production wells through the cement porosity or the cracks in the cement (Al-Ghanim and Al-Nufaili, 2010; Sun et al., 2019). Problems related to near wellbore have been listed below.

1.2.1.1 Problems Related to Casing Leaks

A large diameter pipe is called casing. It is inserted and assembled into the newly drilled wellbore. Deep down in the wellbore, there is no cement to the surface. Due to casing leakage, there is an unexpected increase in produced water as demonstrated in **Figure 1.3a**. These leaks can be classified into two categories: The first one is casing leak with flow restriction and the second one is casing leak without flow restriction. Gel technology may be an effective solution for the treatment of casing leak with flow restriction (Seright et al., 2001).

1.2.1.2 Problems Related to Flow behind the Pipe

Same as casing leakage, also in this problem (flow behind the pipe) two situations contribute. These are flow behind the pipe with restriction and flow behind the pipe without restriction as shown in **Figure 1.3b**. During drilling, a lack of primary cement behind a casing generates a huge aperture, thus producing a highly permeable flow channel (Al-Dossary et al., 2017).

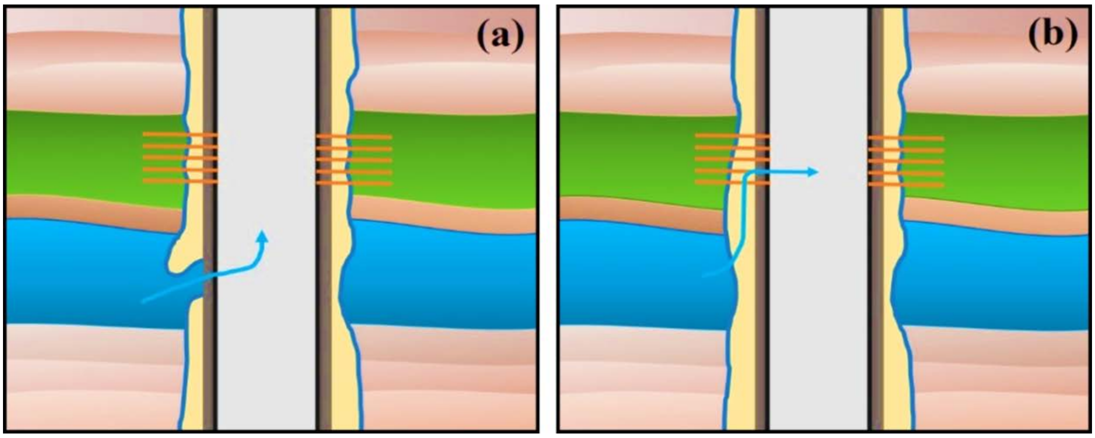

Figure 1.3 (a) Casing, tubing and packer leak (b) Flow behind casing.

Cement shrinkage during the oil well completion is the main reason for the flow behind the pipe with flow restriction. Flow behind the pipe without flow restriction can also be treated using cement. The flow channel is approximately greater than 1/16 inch (Seright et al., 2001).

1.2.1.3 Barrier Breakdowns or Fractures

A fracture can be formed near wellbore either by using acids to dissolve channels or by fracture breaking through a water resistant layer. Water migrates towards wellbore due to the pressure difference across the impermeable layer. Sometimes, this type of issue in the wellbore can be correlated to the stimulation process (Reynolds and Kiker, 2003).

1.2.1.4 Channels behind the Casing

Bad connection between cement and the casing is the main reason for the water channels behind the casing. Cyclic stresses, post-stimulation methods and a bad cementing job may also be responsible for the channels behind the casing. Channeling occurs, when cement is in the annulus but does not completely surround or bonded to the casing. In this condition, there is not a proper blockage for fluid. It leads to a flow of oil, water and gas outside the casing (Jaripatke and Dalrymple, 2010). Space created by the sand may be another cause for the channeling behind the casing. This type of wellbore problem can be treated by using gel or high strength squeeze cement in the casing holes (Bailey et al., 2000).

1.2.1.5 Inappropriate Completion

Well completion is the process in which well (both injection and production) is prepared for production after drilling operations. If well completion is not done by an appropriate method, it can immediately lead to the production of unwanted water. Inappropriate completion of wells may result in coning and cresting at the early stage (Bailey et al., 2000).

1.2.1.6 Scale, Debris and Bacterial Deposits

Scale, debris and bacterial deposits can block or modify the flow of injected water to undesired zone (Jaripatke and Dalrymple, 2010).

1.2.2 Reservoir Related Problems

During oil production from the oilfields, the production of water is an expectable outcome. Control of produced water at the early stage of production is not possible. After secondary recovery, many thermal and non-thermal methods are used to control excess water production (Bailey et al., 2000). Six reservoir related problems have been listed below.

1.2.2.1 Fissures between the Injection and Production Wells

When water or gas is injected into injection wells to maintain reservoir pressure, it breaks through one or more production wells, which is called water or gas breakthrough. It can cause excessive water production through production wells thus lowering the production of oil. Fissures present between injection and production wells are the main reason for early stage water breakthrough. It is demonstrated in **Figure 1.4a** (Bailey et al., 2000). Gel treatments are the best methods to treat these fissures because gelants can be easily penetrated into these fissure zones (Bailey et al., 2000).

1.2.2.2 Coning and Cresting

Coning is a production well related problem that occurs when gas from cap gas or bottom water penetrates in the perforation zone of near wellbore. Water coning should not be mixed up with excess water production because excess water production is referred to as higher water to oil ratio. Vertical and horizontal wells show different types of shapes of coning, as shown in **Figure 1.4b.**

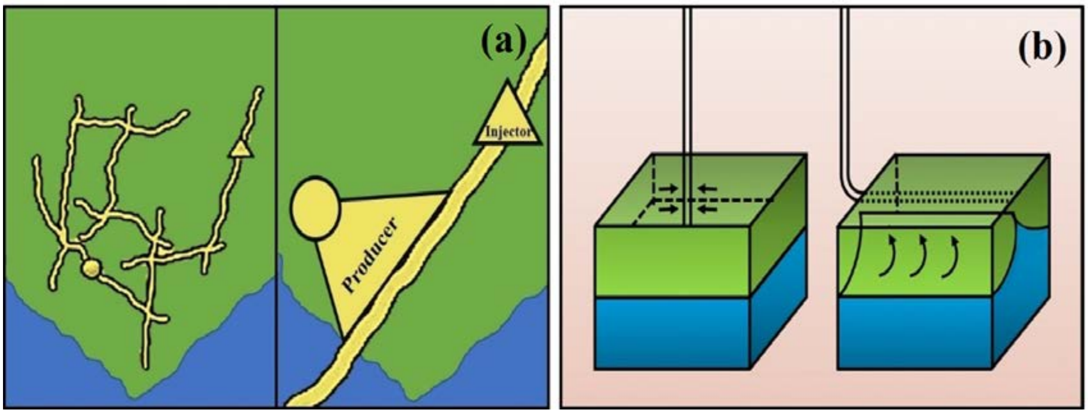

Figure 1.4 (a) Fissures between injector and producer (b) Water coning in vertical and horizontal.

The coning interface shape is like crest in the horizontal well. The horizontal wellbore produces a smaller amount of excess water in comparison to a vertical wellbore. The oil recovery will greatly be affected after coning into the production interval, which will also lead to a dramatic rise in the water and gas production rate (Bailey et al., 2000).

1.2.2.3 Channeling through High Permeability Zones

A high permeable zone provides a path to injected water for easy flow towards the production well, that condition is called breakthrough. The low permeable channel will be bypassed by the injected fluid and it flows through the high permeable zones in between injected and production well. This activity leads to poor sweep efficiency and high water to oil ratio. The main reason for channeling in high permeable zones is reservoir heterogeneity (Bailey et al., 2000).

1.2.2.4 Fingering

In the oil reservoir, viscous fingering is the unstable movement of the injected fluid by the displaced fluid. This fingering of water into reserved oil can greatly influence the flow of water in high permeable zones and can lead to poor sweep efficiency during the recovery of oil. Sometimes fingering also occurs in the absence of a porous medium (Kargozarfard et al., 2019).

1.2.2.5 Watered-out Layer with and without Crossflow

Watered-out with and without crossflow is exposed in **Figures 1.5a and 1.5b.** During oil recovery in the multi-layered reservoirs, a different pressure gradient is produced through the surface of each permeable layer. This pressure gradient generates driving forces in the wellbore during well shut-in that leads to movement of displacing fluid from high to low pressure permeable layer. This phenomenon is known as crossflow. Crossflow behavior depends upon the initial pressure in the permeable layers or it may be addressed as natural crossflow. Crossflow may result in formation damage, filter cake build-up, permeability reduction in low permeable zones and induction of sand liquefaction and production in high permeable zones (Jalali et al., 2016).

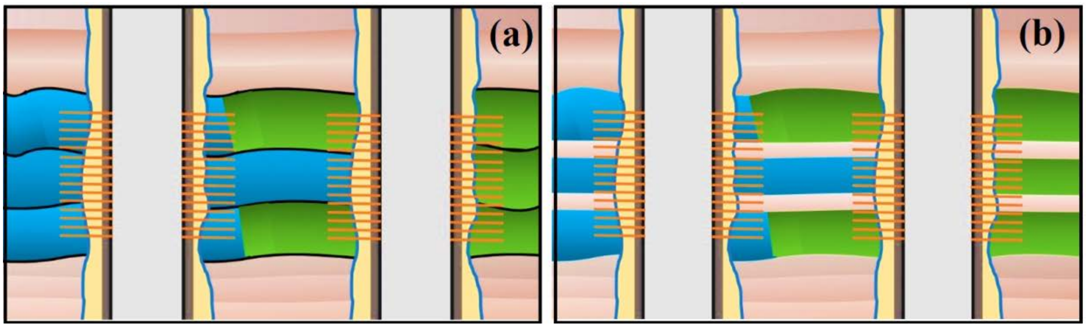

Figure 1.5 Flow of water (a) with crossflow and (b) without crossflow.

The water-out layer without crossflow is also a common problem. This type of problem is easily associated with multilayer production in a high permeability zone with impermeable barriers isolation. This problem is easy to treat; either a rigid shut-off fluid or a mechanical method can be applied in either injection wells or producing wells (Bailey et al., 2000; Bybee, 2009).

1.2.2.6 Fracture Zones

Fractures are the main reason for reservoir heterogeneity. These zones can extend over hundreds of meters to many kilometres and vary in width from just a few fractures close to each other up to many tens of meters. Fractures are of two types, which are natural and hydraulic fractures. It is shown in **Figures 1.6a and b.**

Formation damage of a fractured reservoir due to drilling and completion fluid enters the fracture. Drilling and completion fluid can easily enter fractures in comparison to the pores of the matrix. Gel technology may be a successful tool for treating these reservoir problems (Bailey et al., 2000).

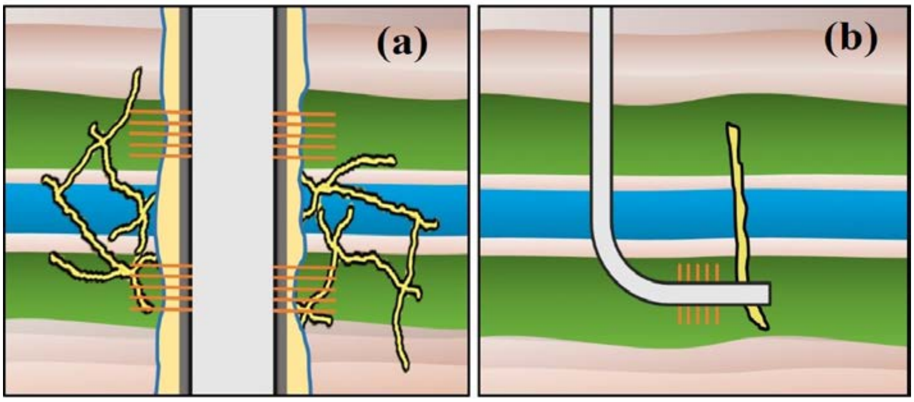

Figure 1.6 Fractures or faults from a water layer surrounding (a) vertical well (b) horizontal well.

1.3 Problems Based on Treatment Difficulty

Oil and gas production are growing and the demand for those fuels is increasing day by day. According to the water online report, oil production will increase to 100 million barrels per day by 2035 worldwide (Water online report, 2014). Different types of produced water are shown in the flowchart (**Figure 1.7**).

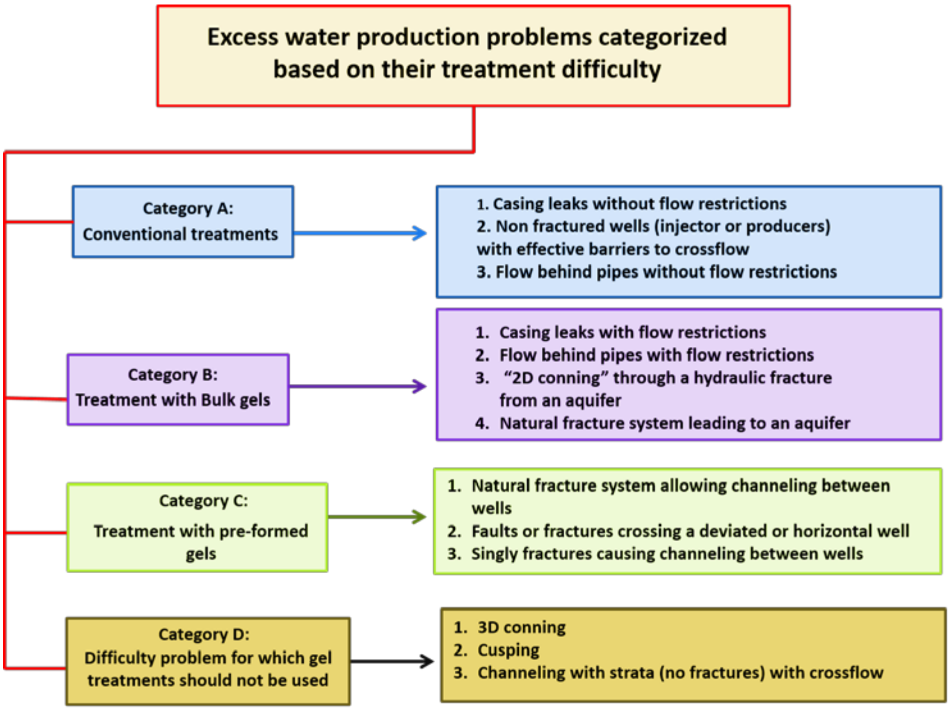

Figure 1.7 Flowchart for produced water problems categorized based on their treatment difficulty.

1.4 Produced Water Control Techniques

There are several methods to control the excess water production problems associated with EOR methods (Kabir, 2001; Sun and Bai 2017a; Taha and Amani, 2019). This produced water is responsible for the early stage maturation of the oilfields. Mechanical and chemical methods are widely used for controlling excess water in the oil and gas industries.

1.4.1 Mechanical Methods

Mechanical methods are generally used to control coning produced water using downhole separation and disposal, drawdown reduction and coproduction. The most commonly used mechanical methods are (i) straddle packers (ii) tubing patches (iii) bridge plugs (iv) sand plugs (v) expandable tubular and (vi) cementing. These methods are least used nowadays because of their expensive nature.

1.4.2 Chemical Methods

Presently, chemical methods are the best alternatives (Kabir, 2001). The use of polymer gels for water shut-off purpose is one of the best methods come under chemical methods. These gels are used for controlling excess water during oil recovery (Kabir, 2001; Taha and Amani, 2019). These gels can be injected into oil well using the rig, making these systems more suitable for the operation and these chemical methods are less expensive (Hayatullah et al., 2015; Soliman et al., 2000). When gel solutions are injected, they penetrate deep down in the reservoir. After allowing gel solutions sufficient time to stay in the reservoir, they form a three-dimensional structure there.

Present research is based on polymer and nanocomposite gels. Polyvinyl alcohol and polyvinylpyrrolidone polymers have been chosen for making gels due to their cost- effective nature and very low viscosity.

Polymer gels are water soluble polymers crosslinked with organic and inorganic crosslinkers. Gel systems have attracted wide attention due to their effectiveness in porous media. These are very helpful in blocking high permeable zones and diverting injected water into low permeable zones (Alghazal and Ertekin, 2018; Zhu et al., 2017). Three types of gels are used for water shut-off and enhancing oil recovering factor purposes. These gels are in-situ gels, preformed gels and foamed gels. The present work is on using in-situ gels. Different types of gels are summarized in the flow chart given below (**Figure 1.8**).

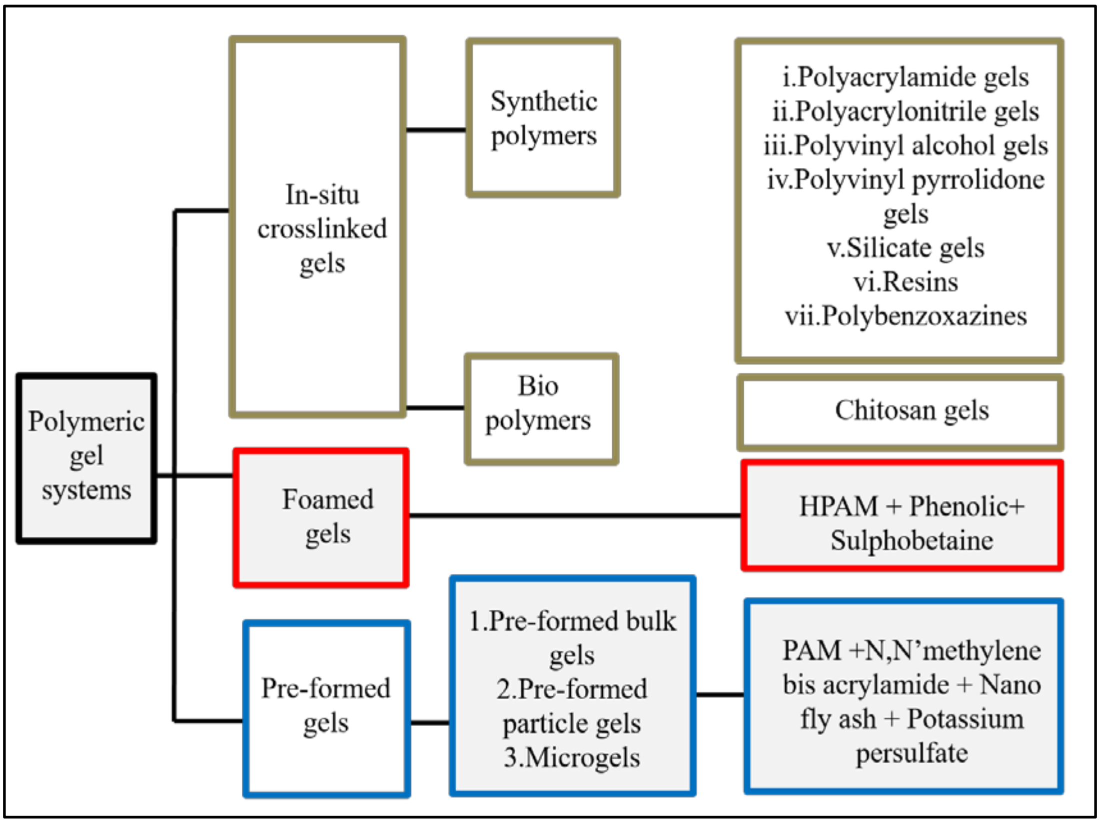

Figure 1.8 Classification of different types of gels.

1.5 Factors Affecting In-situ Gelation

The process of forming gel from a gelling mixture in the porous media is called in-situ gelation. It is known that numerous variables contribute to influencing gels characteristics such as viscosity, gel time and gel strength. Other variables, which also affect gelation kinetics much include reservoir temperature, initial pH, the concentration of polymer and crosslinkers, salinity of the fluid, etc. (Al-Hajri et al., 2019; Baojun et al., 2004).

1.5.1 Effect of Polymer Concentration

Polymer concentration is an important factor in preparing gel. Polymer solution should be of low concentration because highly concentrated polymer solution cannot be easily injected in the oil well. Polymer properties such as viscosity, moisture content, etc. are important to measure during the preparation of the polymer solution. Gel strength of a gel system can be measured using the bottle testing method because it is a cheap and fast method. Free flowing to ringing rigid gel can be coded as A to J according to strength. Code A is for free-flowing gel and J for ringing rigid gel or alternatively, it can be described as an increase in strength of the gel is observed from A to J gels (Sydansk, 1990). From many studies, it has been concluded that increasing polymer concentration, gel strength increases and gelation time decreases (Al-Hajri et al., 2019; Baojun et al., 2004).

1.5.2 Effect of the Crosslinker Concentration

Crosslinker concentration also affects the gel strength. Crosslinker causes the bonding between polymer and crosslinker. Inorganic and organic both types of crosslinkers are used for crosslinking in gels. Inorganic crosslinker forms ionic bond while organic crosslinker forms a covalent bond. From many studies, it has been concluded that increasing crosslinker concentration gel strength increases and gelation time decreases (Mashhoor et al., 2011; Sengupta et al., 2012; Yadav and Mahto, 2014). On using a very high crosslinker concentration, polymer chains are assembled at a place that leads to gel shrinkage and syneresis occurs in the gel system (He et al., 2015; Xiong et al., 2018).

1.5.3 Effect of Temperature on Gelation and Gel Strength

Temperature is also a very important factor to consider during gel preparation. The temperature has a significant impact on the oil recovery. Gelation time is known as a function of polymer and crosslinker. On increasing temperature, gelation time decreases and gel strength increases. Increasing temperature, mobility of polymer chains increases, and the formation of new bonds takes place very easily, which leads to high gel strength of the gel. The gelation time is correlated to the temperature according to the Arrhenius equation:

$$K = K_0 e^{\frac{-E_a}{RT}} \qquad \text{..... (i)}$$

Where, k is the reaction rate constant, K_0, frequency factor, E_a, energy of activation (KJ/mol), R, the gas constant (KJ/mol.K) and T, the absolute temperature (K).

Equation (ii) given below is modified by introducing the gelation time (GT) instead of the reaction rate constant K and M as the frequency factor.

$$GT = M e^{\frac{E_a}{RT}} \qquad \text{.....(ii)}$$

Where, GT is gelation time (h) and M, the rate constant (h).

Equation (iii) can be altered as follows:

$$\ln GT = \frac{E_a}{RT} + \ln M \qquad \text{..... (iii)}$$

As we can see from equation (iii), there is a linear relationship between ln GT and the inverse of temperature (1/T) (Singh and Mahto, 2018a). According to the above equation, on increasing temperature, gelation time decreases (Liu et al., 2019; Zhao et al., 2015).

1.5.4 Effect of Salinity

Salinity is one of the main influencing factors, which highly affects the gelation time and gel strength. Gels prepared in deionized water or distilled water show good gel strength. Mono and divalent ions are generally used to check the salinity effect on gels. On increasing concentration of mono and divalent ions, these are assembled around the functional groups of polymers, which cause the shrinkage of the polymer chains. It hinders the bond formation between polymer and crosslinker (Zhao et al., 2015; Llamedo et al., 2005). The high concentration of salt leads to a decrease in gel strength and increases gelation time.

The presence of calcium and magnesium ions has a more negative effect on gel strength than sodium and calcium. These are divalent ions, when these are assembled around polymer functional groups, due to the large size of ion crosslinking rate becomes very low as a result gel strength lowers much more than monovalent ions. (Jia et al., 2016; Zhang et al., 2017).

1.5.5 Effect of pH on Gel Strength and Gelation Time

Gu and co-workers have done a comprehensive study of the pH effect on gel strength and gel stability (Gu et al., 2015). During this study, it was observed that at pH 4, viscosity of the system has no significant difference with the pure polymer solution when the crosslinker solution is not added. The main reason for low viscosity of gelling solution at lower pH may be due to the excess of hydrogen ions in the gelling solution. Since the more hydrogen ions are present in the gelling solution, hydrogen ion dissociating from the carboxylic group of the polymer is curbed. At lower pH value, the carboxyl group is protonated. It leads to less interaction of polymer chains with the crosslinker (Patzek, 1996).

It was observed that a favorable reaction may occur in the pH range of 8-9 because at high pH, carboxyl groups are deprotonated. The deprotonated carboxyl group (COO^-) leads to more interaction with the crosslinker. Higher pH of the gelling solution gives more interactions between polymer and crosslinker. Therefore, when pH is alkaline, the viscosity of the gelling solution is higher than the viscosity of this solution under acidic conditions. pH also affects the speed of gelation (Xiaofen et al., 2009). So, there are lots of amide and carboxylic acid groups to react with the crosslinker. Many other researchers also studied the effect of pH on gel stability (Karimi et al., 2014; Mohammad et al., 2007; Sengupta et al., 2012; Singh and Mahto, 2018b).

1.5.6 Effect of Pressure

Pressure does not have a substantial influence on the gelation kinetic (gelation time and gel strength). Sydansk has reported that the gelation rate is a weak function of pressure and increases slightly with pressure (Sydansk, 1987). Mohammad and co-workers studied the effect of pressure on the gelation kinetic and observed that gelation time was around 5 hours for all samples. It was noted that the final viscosity is unaffected to pressure. When the pressure was increased by a factor of 10, the final viscosity was increased by a factor of only 1.25 (Mohammad et al., 2007).

1.6 In-situ Polymer Gels for Improving Sweep Efficiency and Water Control Treatments

As mentioned above, crosslinked polymers systems are used in reservoirs to increase volumetric sweep efficiency both for mobility control and in-depth conformance control. Employment of water soluble polymers for improving recovery of oil with the main functionality of expanding the viscosity of the displacing liquid, water was first recommended more than fifty years ago. After that, this work was further directed then trailed to recognize the profits using non-Newtonian displacing fluids in oil recovery applications (Zallaghi et al., 2018; Zeinijahromi et al., 2015). These gels are used for controlling water coming out from hydrocarbon reservoirs during production (Wei et al., 2014). The mechanism behind the enhancement of oil recovery using monomer or polymer gels is based on decreasing the mobility difference between displacing (water) and displaced (oil) fluids. Several gel systems have been developed using different polymers but a known synthetic polymer is polyacrylamide which played a vital role in making gel solutions and further gels for hydrocarbons industries, which comprise of a carbon-carbon backbone hung with amide groups, possibly tens of thousands of them to provide molecular weights in millions (Almohsin et al., 2019). This polymer, in its pure state, is electrically neutral, seeming to preclude any crosslinking through ionic bonding. However, when mixed with a little alkaline solution such as sodium hydroxide, when subjected to elevated temperature, some of the amides are converted to carboxylate groups. Two commercially known polymers, hydrolyzed polyacrylamide (HPAM) and xanthan gum (a polysaccharide) have also been found to be suitable for oilfield applications. As far as the polymer, HPAM is concerned, it is a water-soluble polyelectrolyte having negative charges on the polymer chains. However, xanthan gum is having remarkable thickening capability, good tolerance to saline atmosphere and temperature (Li et al., 2009; Kalyanarama et al., 2015). The flow of polymers through porous media and their importance in the performance differences of mobility control buffers is reported and claimed by Nogueira (Nogueiraet et al., 2013). While working on the application of polymer gel, the mobility of the displacing phase should be equal to or lower than the mobility of the oil phase. This concept has been extended by (Rashidi et al., 2010; Eoff et al., 2007).

1.7 Objectives

The main objective of this research work is to develop polymeric and nanocomposite hydrogels for controlling the excess water production in the hydrocarbon reservoirs. However, the major objectives of the present investigations are:

- Development of polymeric and nanocomposite hydrogels using different polymers, nanoparticles and crosslinkers.
- Study on the variation in rheological properties of developed polymeric and nanocomposite hydrogels.
- Study on effects of temperature, salinity, polymer concentration and crosslinker concentration on the gelation time and gel strength of polymeric and nanocomposite hydrogels.
- The effectiveness of the developed polymeric and nanocomposite hydrogels under reservoir conditions to control excessive water production in hydrocarbon reservoirs.

CHAPTER 2

LITERATURE REVIEW

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

A thorough literature review of the development of polymer gel systems for water shut-off and enhancement of oil recovery in high or extremely high temperature reservoirs have been reported. Polymer gel systems considered as water control agents have become the most widely applied water management technology to address excessive water production problems and improve oil recovery of upstream hydrocarbon industries (Seright et al., 2002). Several polymer gel systems have been developed keeping the prevailing reservoir conditions of industries but most of the existing developed polymer gel systems are not able to withstand in high temperature and high salinity reservoirs. Karsani et al., 2014 reported a polymer gel for profile improvement and water shut-off jobs. Some detailed study of field application data and chemistry information on the gel treatment were also described, however, this review was not focused on polymer gel systems used for high temperature reservoirs. Those polymer gel systems that can handle high temperature excess water are reviewed. In production wells, where excessive water problems exist, polymer gel systems can be used to plug offended zones or areas (El-Karsani et al., 2014).

In most cases of EOR processes, the reservoir having less than 80°C temperature can be considered as a high temperature reservoir. If the reservoir temperature is higher than 120°C temperature, it can be regarded as an extremely high temperature reservoir (Bryant et al., 1997; Zhu et al., 2017). This is mainly because conventional polymers such as polyacrylamide and xanthan are easily degraded or precipitated above 80°C (Samuelson and Constien, 1996; Caulfield et al., 2002). When the formation temperature is between 60 and 80°C, polymer gels crosslinked by an inorganic crosslinker viz., chromium and zirconium become limited because of pumping problems caused by the short gelation time (Zao et al., 2013). Polymer gels formulated by organic crosslinkers like phenol/formaldehyde and Polyethyleneamine have been broadly applied in high temperature reservoirs (above 80°C) because of the more thermally stable bonds (through dehydration condensation reactions) between polymer and crosslinker compared with that of the inorganic crosslinking polymer gel systems.

Abdulbaki et al., 2014 claimed various polymer microgel technologies for management of water. Polymer microgels are separated into four different types, which are colloidal dispersion gels (CDGs), preformed particle gels (PPGs), temperature sensitive microgels (TSMGs) and pH-sensitive polymer microgels (PSPMGs). There work is principally concerned with the various characteristics such as laboratory experiments, oilfield applications and advantages and disadvantages of the microgels (Abdulbaki et al., 2014).

The objectives of this review is to give an insight of available polymer gel systems used for high temperature reservoirs from the perspective of chemistry and petroleum engineering and to try to provide directions for future studies of high temperature polymer gel systems for water control.

2.2 Enhanced Oil Recovery (EOR)

All recovery methods are described in this chapter. Thermal methods, non-thermal methods, different gel systems, nanotechnology techniques and criteria for polymeric gel treatment have been discussed and reviewed. Different stages in EOR/IOR are shown in **Figure 2.1**. Primary, secondary and tertiary recovery methods are fundamental stages during petroleum production. Primary recovery is the first stage in which crude oil is produced from the reservoir on the natural rise of oil due to pressure difference between the oil field and deep-down reservoir. Gas cap drive, solution gas drive, natural water drive and gravity drainage techniques come under primary recovery. Only 12-15% oil of OOIP is extracted in primary recovery (Gbadamosiet al., 2019; Patel et al., 2014). **Figure 2.2** shows the different oil recovery stages.

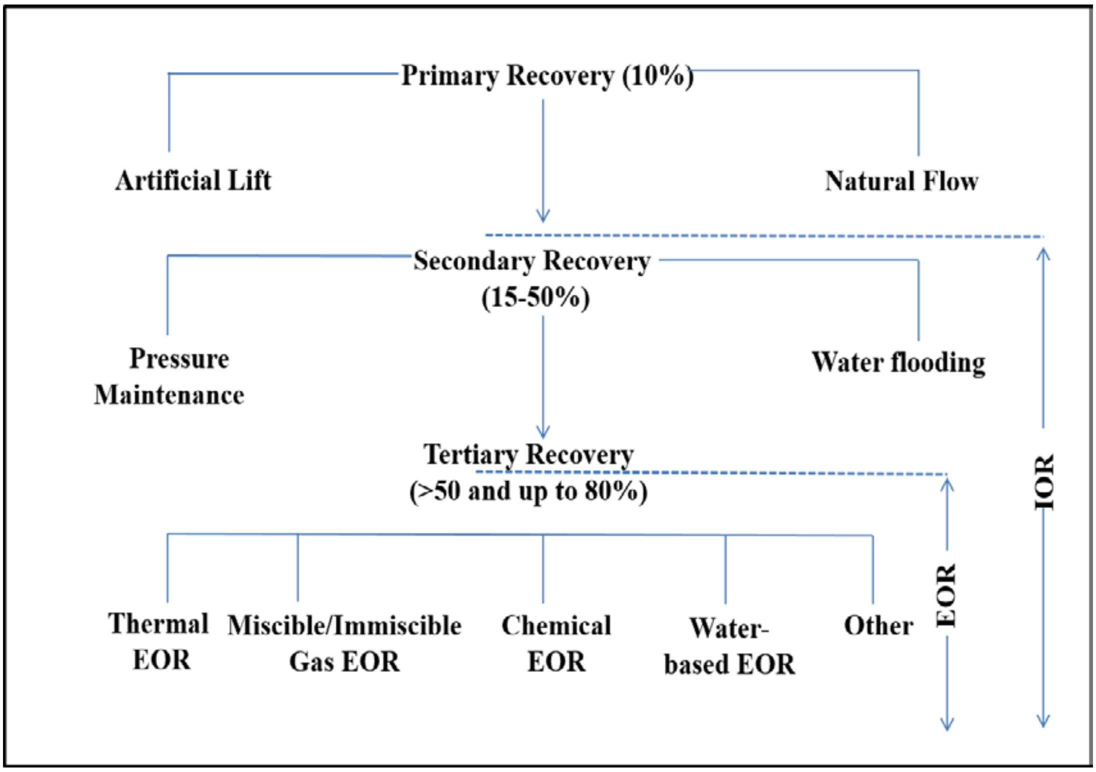

Figure 2.1 EOR/IOR flow chart showing different stages of oil recovery.

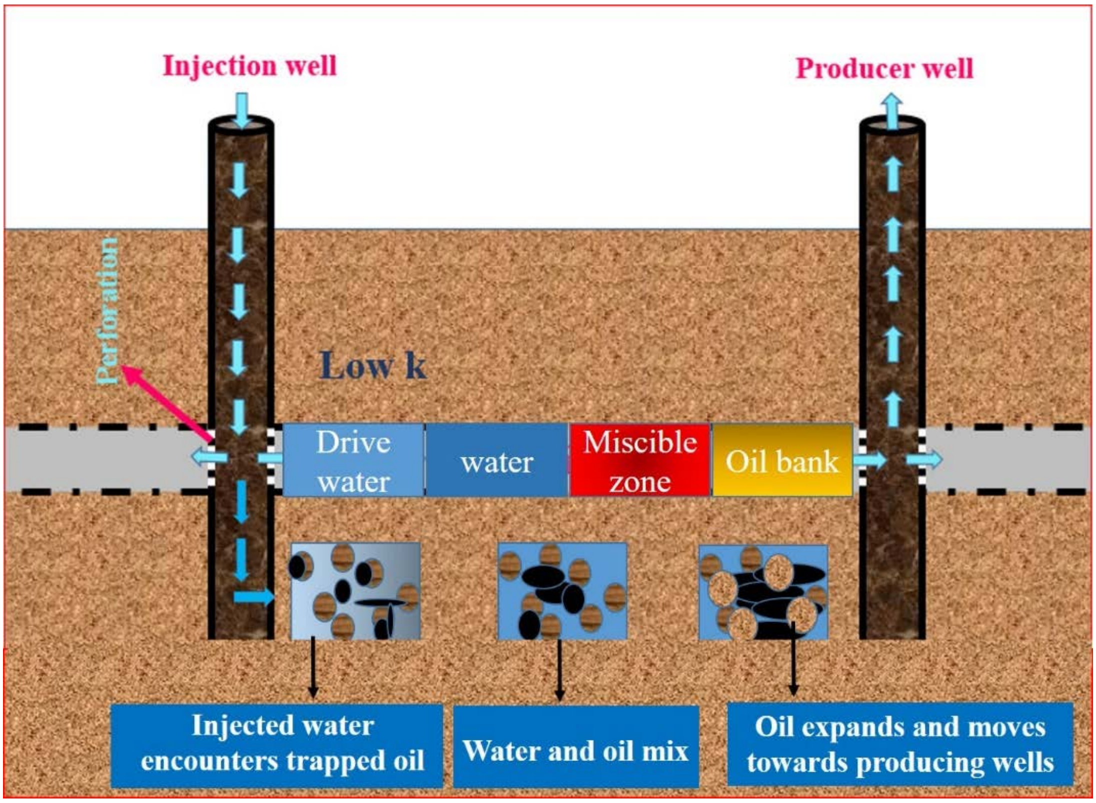

Figure 2.2 Schematic diagram of water flooding in the reservoir and cross-section shows the movement of oil towards producing well after water flooding.

During secondary recovery, an external fluid such as gas and water is injected into the oil wells. The main purpose of this recovery is to maintain reservoir pressure and to displace crude oil into the production well. Generally, water is injected towards the production zone to sweep hydrocarbons from the oil well and gas is injected into the gas cap. The pressure maintenance step can be started during primary recovery. This stage also reaches its limit when water or gas (external driving force) is produced in a considerable amount from the production well. Produced water is not economical for oil wells. After primary and secondary recovery, 20- 45% of oil of OOIP is recovered.

Tertiary recovery is the third phase of oil extraction from the reservoir. It is also known as EOR. In tertiary recovery, 30-60% more crude oil can be extracted from the reservoir compared primary and second recovery (Maroufi et al., 2013; Shih et al., 2018). Energy demand in different regions is shown in **Figure 2.3.**

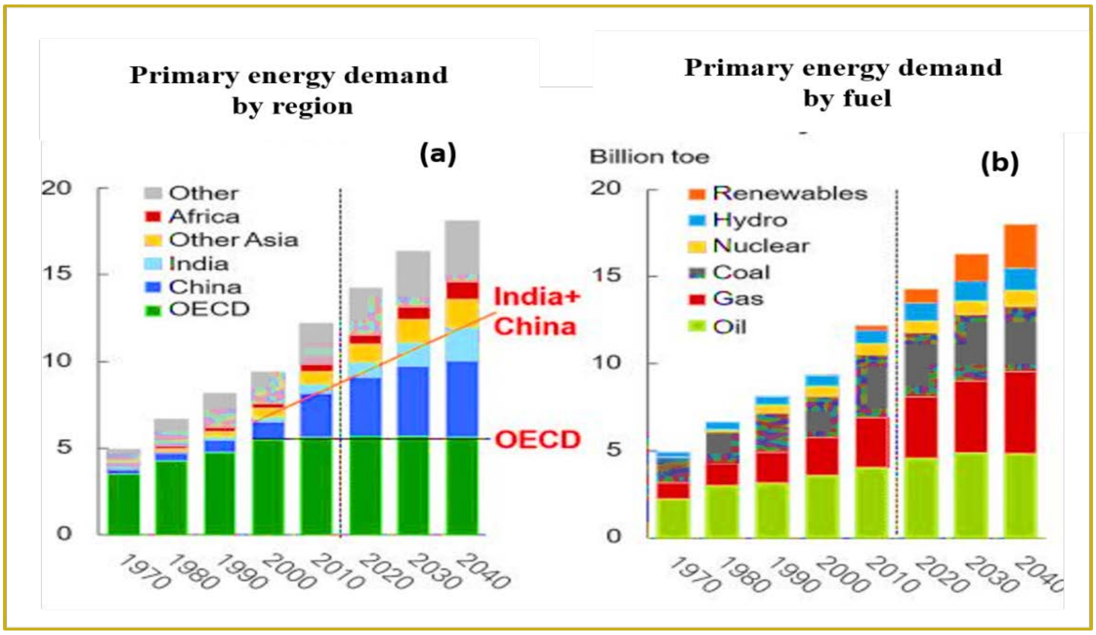

Figure 2.3 Primary energy demand by (a) region (b) fuel of global growth in global energy consumption (Shih et al., 2018).

The lack of energy demand can be compensated by development of certain new gels as well as improving the recovery methods (Alvarado and Manrique, 2010). EOR is the technique of recovery in which some external materials are used from both injection and production wells. These external fluids increase the viscosity of water and simultaneously reduces the viscosity of oil accordingly (Willhite and Green, 1998). In secondary recovery, water and gas are used to push oil from the reservoir. This method of oil production can leave up to 70-80% crude oil in the reservoir. This remaining oil can only be extracted by using tertiary recovery techniques. EOR strategies are influenced by marketing of oil in the petroleum industry. EOR techniques help in maximizing the oil recovery from reservoirs, extend the life of the reservoir and increasing the recovery factors.

Therefore, it can be concluded that EOR proves to be an important technique for the oil industry to maintain oil production. As indicated by the information investigated by the department of energy, the United States still has 649 billion barrels of the total remaining oil in the reservoirs, however, only 22-24 billion barrels is recoverable by ordinary recovery methods. More than 90% of crude oil is still present in the reservoir for extraction (Babadagli, 2020). A report of EOR methods based on 1507 projects around the world is given in **Figure 2.4** (Alvarado and Manrique, 2010).

EOR techniques are categorized into two parts i.e., thermal and non-thermal techniques. Chemical and gas treatments are non-thermal methods. In non-thermal method, chemicals or gases are injected within the reservoir. After allowing enough time, these external forces interact with oil or excessive water accordingly (Henson et al., 2002; Taber et al., 1997). These methods are used to recover the remaining residual oil from the reservoir. Increment in remaining oil production can be increased by reducing interfacial tension, capillary force, oil viscosity and by increasing external fluid viscosity. By changing the mobility ratio, oil production can be increased. As the mobility ratio decreases oil recovery increases or vice versa. Before using EOR techniques there are five main reservoir issues to consider (Zheng et al., 2011). These issues are high residual oil, high oil viscosity, heterogeneity reservoir, reservoir fracture problems, and oil-wet rock. **Figure 2.5** illustrates five main reservoir issues.

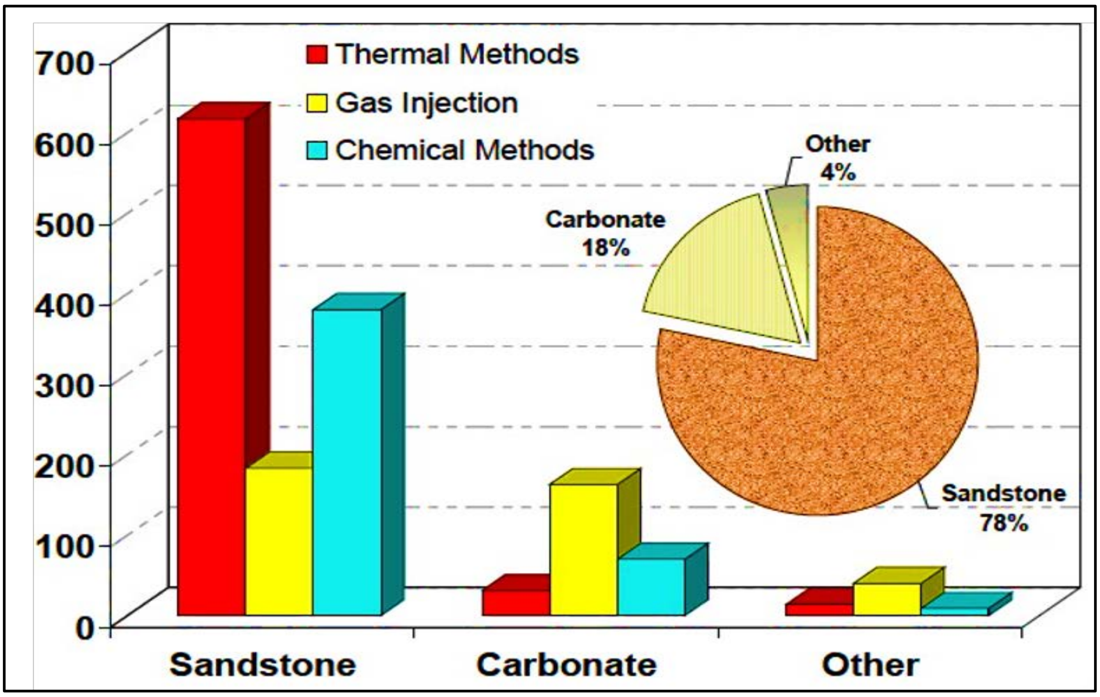

Figure 2.4 EOR report based on 1507 projects around the world (Alvarado and Manrique, 2010).

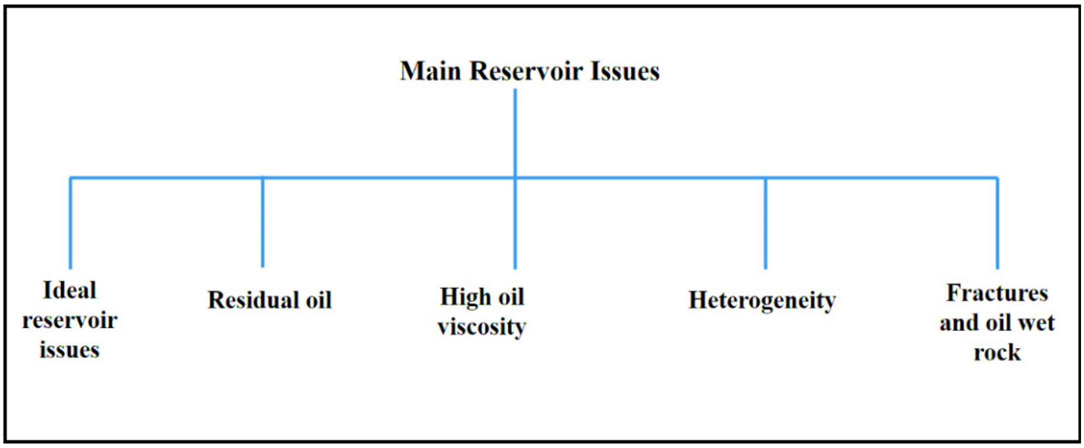

Figure 2.5 Five main reservoir issues.

When the oil viscosity within the reservoir is higher than the displacing fluid, the fingering of that injected fluid takes place. Heterogeneity in reservoirs is the fundamental reason for less oil production because displacing fluid goes from high permeable zones rather than low permeable zone (Gbadamosi et al., 2019). Fractures in oil reservoirs is also a reason for low oil production. These fractures have naturally occurred in the reservoir. This phenomenon generally occurs in carbonate reservoirs. Oil-wet rock phenomena lead to more residual oil left in the oil wells (Zaeri et al., 2019). After identifying these reservoir problems, different EOR methods are applied (Willhite and Green, 1998).

Polymer flooding, micellar-polymer flooding, alkaline flooding, and gel treatments are the important techniques used for water shut-off jobs. Chemical treatment is the most useful EOR method according to the field database report (Al-Shakry et al., 2018; Das et al., 2017; Pei at al., 2012). In micellar- polymer flooding, an aqueous solution of the micelle is injected into the reservoir to minimize interfacial tension between oil and water. Micelle solution is used along with a polymer solution. This solution has an advantage of increasing both volumetric sweep efficiency and oil displacement (Dang et al., 2014). Alkaline flooding is an enhanced water flood method in which the pH of displacing flood is changed. It changes the mobility ratio and helps in more oil recovery. The pH of displacing water can be changed by adding sodium hydroxide (NaOH) or sodium orthosilicates. In alkaline surfactant flooding, petroleum acids and alkaline chemicals are used to form surfactants. This flooding helps in minimizing interfacial tension between oil/water, and wettability (in term of oil) of rock surfaces (Sadati et al., 2019; Willhite and Green, 1998).

Polymeric gels are used to block high permeable zones in the reservoir and alteration of displacing fluid in low permeable zones. Nowadays, a new type of polymer gels based on bright water and colloidal dispersion is used to effectively control the excess water production. Alkaline surfactant flooding has great prospects for enhancing oil recovery of heavy crude oil due to the synergistic effect between micelles and alkaline solution (Ge et al., 2012; Phukan et al., 2019).

2.3 Polymer Gel Technology for Controlling of Excessive Water Production

Hydrogels composed of polymers and crosslinkers are most commonly used in hydrocarbon industries. These are cost-effective and helpful in controlling excessive water production (El-Karsani et al., 2015; Hasankhani et al., 2018).

In polymer gel treatment, the aqueous solution of polymer and crosslinker is used. The solution of these two materials is made and injected into the injection and production wells to form gel. Thereafter, the well is shut-off for a certain time period. After allowing sufficient time, a three-dimensional gel network formation takes place. Subsequently, water is injected into the reservoir to determine permeability, which is an important parameter for water control and EOR. The reaction between polymer and crosslinker is shown in **Figure 2.6**.

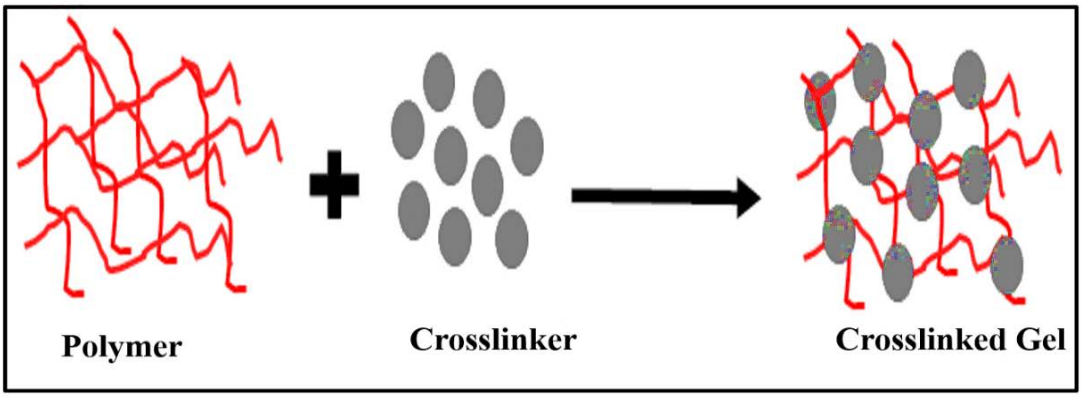

Figure 2.6 Three-dimensional solid-like structure of crosslinked polymer gel.

The settled gel within the high permeable region of the reservoir could obstruct the flow of water in blocked or high permeable zones. The blocking of high permeable zones and alteration of displacing fluid in reservoir is shown in **Figure 2.7** (Zhu et al., 2017).

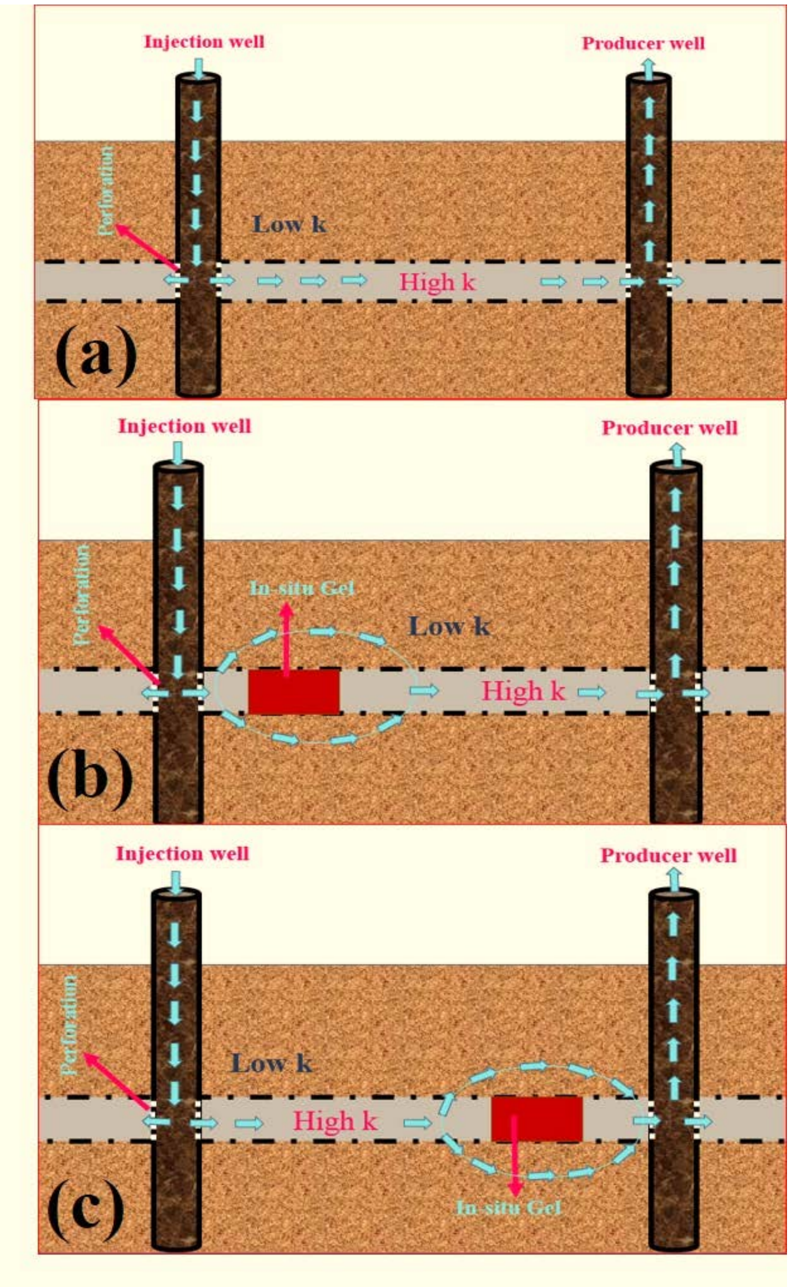

Figure 2.7 Schematic of excessive water production problems and its management mechanism by using gel systems (a) Excessive water production (b) Profile control from the injector (c) Water shut-off from the producer (Zhu et al., 2017).

2.4 Classification of In-situ Crosslinked Polymer Gels for Water Shut-off

Gel injection is one of the most important chemical methods for water shut-off operations. Gel treatments not only help in enhancing oil recovery but also decrease the operational costs associated with oil and water separation. Polyacrylamide (PAM) polymer is generally used in preparing gels for water shut-off purposes. Both inorganic and organic types of crosslinkers are used for the crosslinking of polymers (El-Karsani et al., 2015 Hasankhani et al., 2018; Sultan, 2019). Many other synthetic crosslinked polymer gels are also used for the same purpose using Polyacrylonitrile (PAN), polyvinyl alcohol (PVA), polyvinyl amine (PAMs), etc. Apart from these, some natural polymers are also used for these purposes (Zhu et al., 2017). Reservoir conditions such as temperature, pressure, salinity and pH play a major role in selecting a suitable gel system for a particular oil well. Other than these parameters, the permeability of the heterogeneous reservoir, formation lithology and the salinity of the formation water also affects the formation of gel within the reservoirs (Al-Muntasheri et al., 2012; Zhu et al., 2017). The different crosslinked polymer gel systems, which are employed for the above purpose, are as follows:

2.4.1 Gelation of PAM Polymers (Using Inorganic and Organic Crosslinker)

2.4.1.1 Inorganically Crosslinked PAM Gels

In 1993, Albonico and Lockhart studied the gelation and rheological properties of the polyacrylamide/Cr (III) gel system and found that the gel system has partial control over the gelation time (Albonico and Lockhart, 1993). As a result, the gel deformation takes place at higher temperatures. Thus, the gel is not stable at high temperatures. Some additives such as glycolate, malonate, salicylate, acetate, lactate, etc. can help to resist these gels at high temperatures (Albonico et al., 1993; Lockhart et al., 1994; Salimi et al., 2014).

As far as the use of environment friendly crosslinker is concerned, aluminum based crosslinkers can be used to reduce the toxicity of chromium based crosslinked gels. The polyacrylamide/aluminum citrate gels are successfully used in the diverting flow of injected fluid. These inorganic gels are used for excessive water management in reservoirs with temperatures above 50℃. In many studies, it has been found that aluminum based crosslinkers are not able to crosslink cationic polymers because aluminum itself is cationic in nature (Amir et al., 2018; Bai et al., 2015; El-Karsani et al., 2014).

2.4.1.2 Polyacrylamide/Polyethyleneamine Gels

Polyethyleneimine, which is used as a crosslinker with polyacrylamide, is less toxic than other organic crosslinkers and it is also eco-friendly in nature. These are successfully used in many oilfields globally for the last many years. These gel systems are thermally stable up to a temperature of 135℃ in oil reservoirs. Polyacrylamide/polyethyleneimine gels were used up to 130℃ and 80℃ in carbonate reservoirs and sandstone reservoirs respectively (Al-Muntasheri, 2007 and 2010; Sengupta et al., 2012).

2.4.1.3 Polyacrylamide or Polyacrylamide Tert-butyl Acrylate (PAtBA) /Polyethyleneimine Crosslinked Copolymer Gels

Polyacrylamide or Polyacrylamide Tert-butyl Acrylate (PAtBA) /Polyethyleneimine Crosslinked Copolymer gels are widely used to control produced water in the high temperature reservoirs. Polyethyleneimine crosslinker has been used for the crosslinking of PAM or PAtBA polymers. These gels are thermally stable up to 130℃. It was observed that the rate of crosslinking increases with increase in temperature. After the crosslinking reaction, it was found that the storage modulus was higher at low temperatures. Storage and loss modulus are highly affected by polymer concentration in comparison to crosslinker. Storage modulus decreases on increasing salinity (Al-Muntasheri et al., 2009). Al-Muntasheri and co-workers concluded that samples prepared at acidic and alkaline conditions formed stronger gels than gels formed at neutral conditions concentration (Al-Muntasheri et al., 2009).

2.4.1.4 Polyacrylamide/Phenol-Formaldehyde Gels

A conventional organic crosslinked gel is the crosslinking of PAM, PAM derivatives, polyvinyl alcohol and Polyvinylpyrrolidone with phenol-formaldehyde resin. The gelation occurred through condensation reaction and C-N or C-OH bond formation took place. The reaction takes place between the amide group of PAM, alcoholic group of PVA and –OH group of resorcinol and formaldehyde. Gel systems are thermosets based on the crosslinking reaction between resorcinol-formaldehyde resin and polymers (Jia et al., 2011; Yadav and Mahto, 2013). These gels systems are of very low viscosity, which helps in gel placement within the reservoir. Gelation only appears at neutral or basic pH. At low pH, precipitation formation takes place. Generally, the crosslinking reaction of these gels proceeds in the temperature range between 70-80°C (Albonico et al., 1995; Jia et al., 2016).

2.4.1.5 Polyacrylamide/Hydroquinone-Hexamethylenetetramine (HMTA) and Polyethyleneimine Gels

Polyacrylamide/hydroquinone-hexamine gels are used to overcome the toxicity of phenol-formaldehyde resin. Many derivatives of phenol-formaldehyde such as pyrogallol, phenylacetate resorcinol, catechol along formaldehyde derivatives such as hexamethylenetetramine (HMTA), glyoxal, paraformaldehyde, acetaldehyde, etc. have been used (Fang et al., 2017; Liu et al., 2016). In 1997, Dovan and co-workers developed a new type of less toxic crosslinked gels. These gels were applicable in the reservoirs. Required chemicals were mixed with seawater with 2.0 wt% of sodium bicarbonate. Sodium bicarbonate was used to soften water by precipitating the ions present in seawater and to maintain the pH of the reaction mixture (Dowan et al., 1997). Recently in 2017, Zhu et al., and Sun et al., reported the synthesis of an in-situ terpolymer gel system composed of a terpolymer, resorcinol and HMTA. The gelation and thermal properties of this system were thoroughly studied in literature (Sun et al., 2017b; Zhu et al., 2017). Initially, the hydrolysis of HMTA takes place in an acidic medium. Ammonia and Methyldiol are found as the products. Methyldiol is a very unstable product. Due to unitability, it produces formaldehyde as the final product. This produced formaldehyde reacts with resorcinol or hydroquinone and a condensation reaction takes place. Resin formed in this reaction reacts as a crosslinker for polymers.

2.4.2 Other Synthetic Polymeric Gels

Polyacrylonitrile, polyvinyl alcohol, polyvinyl amine (PVAm) and acrylamide based terpolymer are also used nowadays for water shut-off treatments (Shu, 1997; Zhu et al., 2017).

2.4.3 Gelation of Natural Polymers

Biopolymers have also been used for water shut-off purpose in high temperature reservoirs. These polymers are very less sensitive towards salinity and also very stable at higher temperatures in comparison to synthetic polymers. These polymers can be used for excess water management because of their temperature resistivity and less sensitivity to salt in comparison to polyacrylamide polymer. However, these natural polymers are more vulnerable to microbial attacks. Chitosan, xanthan gum, starch and guar gum are generally used for these purposes (Alquraishi et al., 2012; Amir et al., 2019; Broseta et al., 2000; Yongqiang et al., 2013). These polymers can also be crosslinked with organic and inorganic crosslinkers. Xanthan gum has been widely used in comparison to other existing natural polymers. Xanthan/chromium gel system has been extensively used for water control and flow diversion of injected fluid. Rheological investigations of this system have exhibited shear-thinning behavior (Broseta et al., 2000; Sydansk, 1990). The reaction mechanism of the system exposed that the carboxylic group of xanthan gum and Cr (III) is bonded by the ionic bond (Zhu et al., 2017).

2.5 Nanotechnology

Nanomaterials have been found to be useful in improving polymeric gel properties for different applications. Further improvement in polymer gel properties has been achieved because of the incorporation of nanoparticles within the gel network. In oilfields, polymeric gels are used with metal oxide nanoparticles. These nanoparticles (NPs) enhance gel strength and alters gelation time. The use of nanocomposite gel is one such technology, which is being used to minimize water production from oil reservoirs (Matteo, 2012). The main focus of this part is the use of nanotechnology in EOR to increase oil production. Nanoparticles help in changing the properties of the injected fluid, reduce interfacial tension or oil viscosity, alter the wettability of the porous media. (Alomair et al., 2014; Odedele 2014; Yu et al., 2010).

In carbonate reservoirs, it has been found that more than 60% of crude oil is trapped. The main reason behind this trapped oil is the communication between matrix and reservoir fractures via gravity and capillary forces. It has been seen that the nanoparticles play a promising role due to their capability in altering oil recovery mechanisms and providing a path for trapped oil in the pores within the reservoir (Sun et al., 2017c). Nanotechnology is very helpful in altering specific parameters such as injecting fluid properties and rock properties in order to improve the oil recovery (Negin et al., 2016). Nanoparticles have different properties associated with large particles of the same materials. These nanoparticles have a much greater surface area per unit volume ratio compared to large particles.

Nanotechnology is used when conventional gel systems are unable to produce remaining oil. Various nanoparticles such as Al_2O_3, MgO, Fe_2O_3, SiO_2 containing nanoparticles are widely used in EOR applications nowadays (Ali et al., 2018; Bayat et al., 2014; Moghaddam et al., 2015). Nanoparticle formation is also possible from surfactant because these surfactants show a high impact on the dispersion, nano-emulsions and non-equilibrium systems. These fluids with nanoparticles are called smart fluids for IOR/EOR. These smart fluids contain a very small fraction of nanoparticles. These nanoparticles enhance fluid properties. (Evdokimov et al., 2006). Prepared nano-fluids should be eco-friendly and companionable with reservoir rock. In literature, it has been observed that these nano-fluids showed highly enhanced properties such as drag reduction, helps in maintaining good gel strength, wettability alteration and anti-corrosive coating (Druetta et al., 2018).

2.6 Properties of Nanoparticles

2.6.1 Structural Properties

High surface area per unit volume is one of the important features of nanoparticles. As we know that small particle size of nanoparticles in comparison to large particle size of the same material has more surface area. It is shown in **Figure 2.8**.

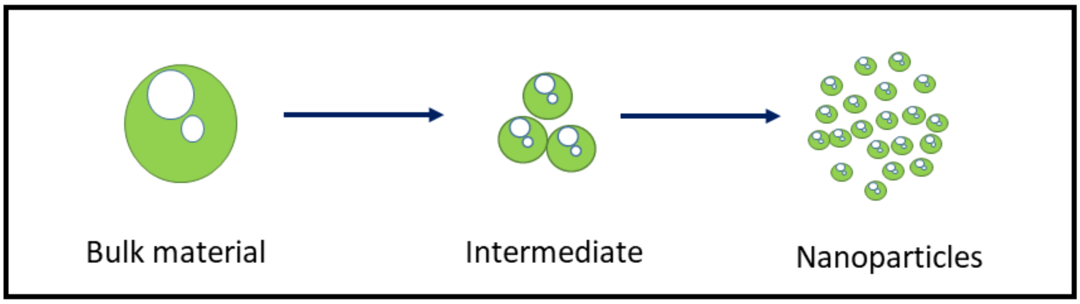

Figure 2.8 Schematic of high surface area to volume ratio (Sun et al., 2017c).

This property leads to a change in the interatomic spacing of the material (Esmaeili et al., 2011). The particle size of nanoparticle ranges between 1-100 nm with a surrounding interfacial layer. This interfacial layer is a part of the nanoscale material and it is responsible for affecting all its properties. This layer is formed by organic, inorganic and ions. These nanoparticles are more stable and useful compared to large particles. Nanoparticles are used in porous media due to more reactivity of these particles owing to their high surface area (Khan et al., 2019; Wynblatt and Ku, 1977).

2.6.2 Chemical Properties

At nanoscale, particles behave very differently as compared to large particles. This change in the behavior of small particles is still very tough to understand. The main characteristics of nanoparticles are their shape, size, the inner arrangement of atoms and surface area (Li et al., 2013).

Nanocatalysis is another rapidly growing field. In nanocatalysis, nanoparticles are used as nanocatalyst in both homogeneous and heterogeneous catalysis applications. The main aim of catalysis is to control chemical reactions by changing the chemical composition, morphological structure, strength of materials, size and dimensions. These particles help in changing the kinetics of the reaction. Nanoparticles allow the rapid, selective chemical transformation with a good product yield. Recovery of catalysts from the reacting system is an important characteristic of any reaction (Abdollahi and Rouhani, 2012; Li et al., 2013).

2.6.3 Mechanical Properties

Nanoparticles provide mechanical properties to materials such as hardness, elastic modulus, interfacial adhesion and friction. Mechanical properties of materials are strongly dependent on the defects present within the materials or the ease of formation. Fewer defects of nanoparticles are responsible for good gel strength of materials (An et al., 2019). Nanomaterials show predominant thermal, mechanical, optical and electrical properties as compared to bulk materials (Guo et al., 2014a). Single-walled carbon nanotubes have shown more mechanical strength than steel due to the presence of these nanoparticles. Nanomaterials are also responsible for changing the behavior of plastic materials. The plasticity of materials can be changed from low to high accordingly by using these small particles. Nanomaterials have properties to undergo deformation without tearing or fracture (Chen et al., 2015; Guo et al., 2014b).

2.7 Nanocomposite Polymeric Hydrogels or Nanohybrids Preparation

Nanocomposite polymeric hydrogels or nanohybrids can be prepared by organic and inorganic methods. The organic method may include the use of monomer, polymer, a linear polymer and a polymer network. The inorganic method can be presented as a nanoparticle precursor and nanoparticle structure (Adnan et al., 2018).

Nanoparticles have stronger affinity for polymers as compared to surfactants and therefore, can bind strongly with polymers. These nanoparticles can help in long time absorption of polymer in the reservoir. This absorbed solution reacts with oil and reduces its viscosity. The enhanced properties of the material can be attributed to good interaction between polymer and nanoparticles (Dannert et al., 2019; Hickey et al., 2015; Hood et al., 2014; Suk et al., 2016). The macroscopic properties of nanocomposites are also influenced by the intrinsic properties of polymers (chain length, linear or branched arrangement of chains, the molecular weight of polymer and elasticity, etc.). Nanoparticles intrinsic properties such as shapes, size, surface characteristics, and inner atomic arrangement highly affect the properties of nanohybrids (Baeza et al., 2016; Lin et al., 2016).

From the literature review of the chemical treatment of NPs in EOR, it has been shown that nanotechnology has the potential to minimize excess water problems and increase oil production. NPs are used with polymer gels within reservoirs due to their ability to alter properties of polymer into the well. The dispersion of nanoparticles with different polymers depends on the functionality of polymer and nanoparticles. NPs exhibit exceptional properties due to their small size and large surface area. Polymer gels of chemical EOR method are characterized using rheology, wettability alteration, interfacial tension and core flooding experiments (Lee and Yoo, 2016; Mullar et al., 2017).

Polymer coated nanoparticles (PNPs) are new materials that may be better to use due to their enhanced solubility in polymer solution and stability, good stabilization of emulsion and foams and long-time absorption in porous media. PNPs are being focused by many researchers for enhancing mobility control, change in surface wettability. PNPs suspensions are also newly developed agents to increase the mobility of oil for EOR in low permeable zones of the reservoir (Flejszar and Chmielarz, 2019; Koschevic et al., 2018).

2.8 Effect of Nanoparticles on EOR

2.8.1 Effect of Nanoparticles on Reservoir Properties

Formation damage is a situation generally produced by wellbore fluids and during several stages of oil production including drilling, well completion, EOR and hydraulic fracturing. During drilling, solid and liquid particles of the mud incline to decrease the volume of pores and effective permeability of the producible formation in the production well. Formation damage can occur near the wellbore or deep into the rock. Formation damage is caused by several reasons including physical plugging of the pore by drilling fluid, alteration in rock wettability, invasion of incompatible fluids, etc. (Agi et al., 2018; Alvarez-Berrios et al., 2018).

Many other parameters such as thermal interaction of rock and fluid, chemical, biological, physical processes are also accountable for formation damage. These above processes may include the formation of damage under stress and fluid shear, permeability damage, skin damage (Mahmoud et al., 2016; Rostami et al., 2019).

2.8.2 Effect of Nanoparticles on Viscoelasticity and Rheological Properties of Polymer Gels

In polymer gel solutions, nanoparticles can strongly alter the storage and loss moduli of the gels. Nanoparticles help in enhancing the viscoelastic properties of gels, which ultimately leads to EOR. Influences of nanoparticles on gelation behavior were thoroughly studied by several researchers earlier (El-Hoshoudy et al., 2017; Ghoumrassi-Barr and Aliouche, 2016). Some nanocomposite gels study is described below.

A starch grafted nanocomposite gel was synthesized, which has shown higher thermal and viscoelastic properties as compared to the conventional gel system (Singh and Mahto, 2017). Polymer, crosslinker and additive effects were also thoroughly studied. Sodium montmorillonite (Na-MMT) nanoparticles were used in this study. Storage modulus increases by two times due to these particles. These nanocomposite gels show higher thermal stability even after 90 days and displayed good salt tolerance as compared with the conventional gel. Coreflooding tests also show 29-38% effectiveness in porous media.

Another nanocomposite gel using nano fly ash and acrylamide was synthesized and reported in 2018 (Singh and Mahto, 2018a). Chromium acetate was used as a crosslinker in the system. The hydrogel was synthesized using free radical polymerization. Effect of various parameters like polymer, crosslinker, nano fly ash concentration, temperature, etc. was evaluated using a breakthrough vacuum method. It was reported that nanocomposite gel has good gel strength and gelation time as compared to the conventional gel system.

Michael and co-workers studied the effect of zirconium hydroxide ($Zr(OH)_4$) on the PAM/HQ-HMTA gel system (Michael et al., 2018). In their research, they have highlighted the effect of nanoparticles on thermal and rheological properties. The change in thermal and rheological properties due to nanoparticles is shown in **Figure 2.9.**

Recently in 2017, Liu and co-workers investigated the effect of silica nanoparticles (SiO_2) on the polyacrylamide/hydroquinone-hexamethylenetetramine gel system. The crosslinking reaction is depicted in **Figure 2.10.** They evaluated the effect of SiO_2 on the gelation performance of gel. Finally, they observed that gel time decreases, and gel strength increases in case of nanocomposite gels in comparison to conventional gels (Liu et al., 2017).

Another investigation was conducted for observing the gelation behavior of sulfonated polyacrylamide nanocomposite hydrogel in the year 2014 (Salehi et al., 2014). Plackett-Burman method was used for testing a large number of factors such as polymer concentration, crosslinker concentration, nanoparticle concentration, salinity, temperature, pH, etc. The two experimental procedures for the optimal hydrogel have been shown in **Figure 2.11.**

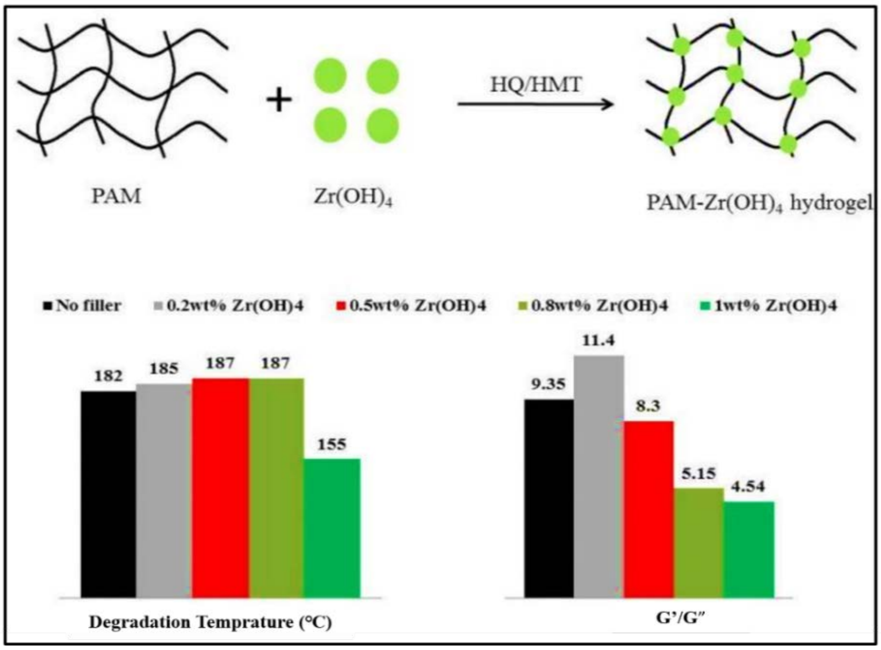

Figure 2.9 Effect of $Zr(OH)_4$ on thermal and rheological properties of gels (Michael et al., 2018).

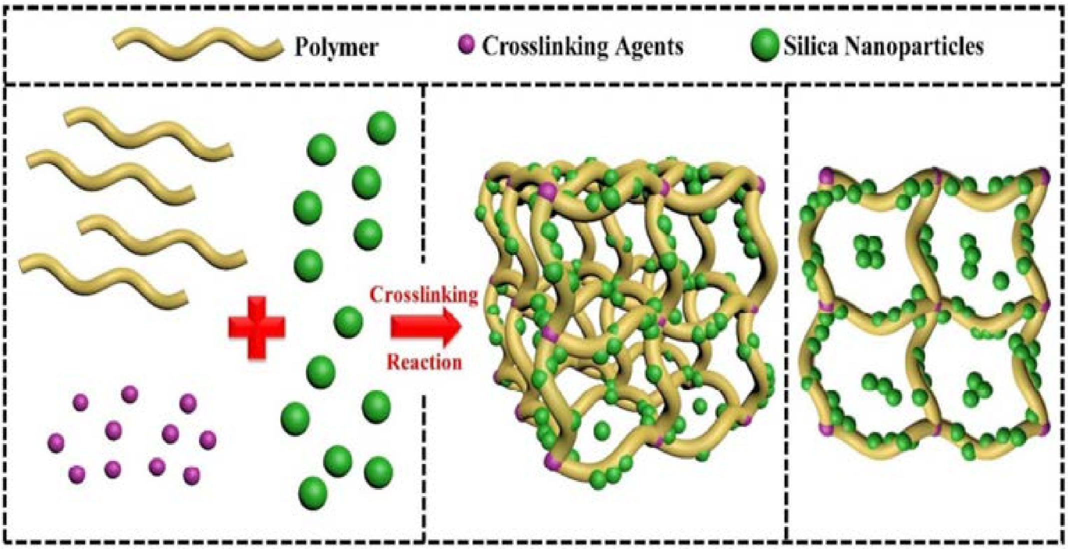

Figure 2.10 Mechanism of polymer and nanoparticle interaction (Liu et al., 2017).

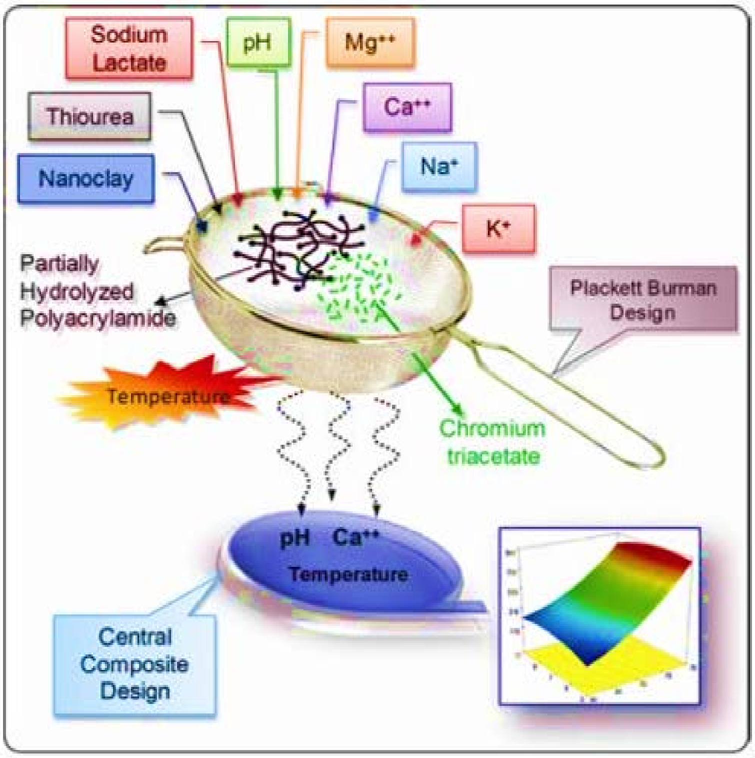

Figure 2.11 Schematic of the experimental procedure including Placket-Burman and central composite design (Salehi et al., 2014).

2.9 Conclusions

The following conclusions were drawn from the literature review of polymeric gels:

- The flexibility of gels can be altered by changing the concentration of polymer and crosslinker.
- On using a high concentration of polymer and crosslinker, mechanical strength of gels decreases and rises the possibility of syneresis of gels.
- Both the types of gels i.e., conventional and nanocomposite, have engrossed a high consideration due to their excellent thermal properties, rheological properties and good effectiveness in porous media.

- The gelation time, mechanical properties, thermal properties and in-situ gelation study were the important parameters during the synthesis of these gels.
- Results from the polymer and nanocomposite gels are very promising and they can be successfully used for water shut-off treatments in the hydrocarbon reservoir.

CHAPTER 3

EXPERIMENTAL PROCEDURES AND TECHNIQUES USED FOR CHARACTERIZATION

CHAPTER 3

EXPERIMENTAL PROCEDURES AND TECHNIQUES USED FOR CHARACTERIZATION

3.1 Introduction

Oil and gas production are typically hindered by the formation water in the hydrocarbon bearing reservoirs. This formation water can enter the production zones through fractures already existing in the reservoirs, which causes problems such as corrosion of the reservoir facilities. This along with reduced oil and gas production ultimately ends up in damage and earlier shut-off the wells. Efforts are being directed to control water and billions of dollars are spent to minimize produced water because of environmental problems and provisions of environmental regulations. An approach to save on treatment costs of this produced water is to apply water shut-off treatments (Al-Muntasheri et al., 2007; Sharifpour et al., 2015). At the present time, produced water management has become an important concern for hydrocarbon industries. Several methods are considered to be used for controlling water. Among them, there are three common methods, which are helpful in improving water shut-off performance, which increase the viscosity of the flooding fluid, reduces the permeability of high permeable streaks present in the reservoir and increase the permeability of low-permeable zones (Zhu et al., 2017).

Among all water control processes, chemical water shut-off treatment is one that has shown potential feasibility and practicality in hydrocarbon reservoirs for decades. The polymer gel system, which is formed after the crosslinking reaction between polymer and crosslinker, is one of the most promising water shut-off agents because of its low price, easy method of preparation, pumping and effectiveness (Zhao et al., 2014).

Field applications have confirmed that polymer gel treatments can be applied successfully in heterogeneous reservoirs to minimize excess water production (Goudarzi et al., 2014). Field studies have also demonstrated that gel formulation, gelling fluid or gelant is supposed to form a three-dimensional molecular network within the porous media of the reservoir. The effectiveness of water shut-off treatment depends on the compatibility of the gel formulation with harsh reservoir conditions as well as the appropriate placement of the gelant in excessive water zones because the gel network blindly blocks any zone, which is treated by the gelant (Elewaut et al., 2005; Wassmuth et al., 2004). Polymer gel systems are usually composed of a water-soluble polymer or monomer crosslinked with an organic or inorganic crosslinker. Polymer gels, which are crosslinked by inorganic crosslinkers such as zirconium and chromium containing crosslinker, become unsuccessful when reservoir temperature reaches above 80ºC temperature. To overcome this issue, polymer gel systems with organic crosslinkers are considered the best and preferred everywhere. Polyethyleneimine and phenol/formaldehyde have been largely used in high temperature reservoirs. This selection is contributed by the existence of thermally stable bonds within the organic crosslinked polymer gel system (Amir et al., 2019; El-Karsani et al., 2014; Moradi-Araghi, 2000; Zhu et al., 2017). Three different types of gels are used for water shut-off purposes in the reservoir. The first type of polymeric gel systems are in-situ gel systems, however, second and third types form particle gel and foamed gels respectively for the purpose (Ganguly et al., 2002; Imqam and Bai, 2015; Sydansk, 1990).

In 1989, PVA crosslinked with phenolic derivative and aldehyde gel system was developed and reported. This crosslinked PVA gel system was an effective permeability control agent, which was found to be stable even at high underground formation temperatures. PVA is a well-known commercially available polymer, which is prepared by substituting acetate groups of polyvinyl acetates with hydroxyl groups (Hoskin and Shu, 1989). Shu again, in the year 1997, developed a polymer gel system using derivative of PVA i.e., polyvinyl alcohol-co-vinyl amide copolymer (PVOH-VAM), the crosslinking agent maloaldehydebis (dimethyl acetal) and maloaldehydebis (diethyl acetal) along with a strong base for adjustment of the desired pH of the system (Shu, 1997). Another similar system, PVA crosslinked with methylated melamine-formaldehyde resin, has also been developed and reported for the same purpose (Victorius, 1991).

Polymer blending is one of the most important and recent methods for the development of new polymeric materials. The significant advantage of the polymer blend is that the properties of the final product sometimes can be more useful than that of an individual polymer (Abdelrazek et al., 2010). Polyvinylpyrrolidone has a good reputation due to its outstanding absorption and complex forming abilities, whereas polyvinyl alcohol presents important features such as high hydrophilicity and good capacity of film formation (Bernal et al., 2012).

Polyvinylpyrrolidone is a vinyl polymer possessing planer and polar side groups due to the peptide bond in the lactam ring (Mayo-Pedrosa, 2004). It is an amorphous polymer and possesses high glass transition temperature (T_g) because of the presence of the rigid pyrrolidone group, which is strong in drawing the group and is known to form various complexes with other polymers. On the other hand, PVA is a semi-crystalline polymer studied extensively because of its numerous interesting physical properties, which arise from the presence of –OH group and the hydrogen bond formation. When these two polymers are mixed, the interaction between PVA and PVP are expected to occur through inter-chain hydrogen bonding between the carbonyl group of PVP and the hydroxyl group of PVA. Hence, these hydrogel blends are stable within the physiological environment because of physical crosslinks consisting of intermolecular hydrogen bonds (Queiroz et al., 2001). The crystallinity of PVA/PVP blend decreases with increasing the level of PVP (Zidan et al., 2016). PVA has analogous properties like PVP but it varies in some properties like good tensile strength and elasticity (Tian et al., 2017; Tian et al., 2018; Yan, 2015). Due to these special properties of PVA, it works well with another polymer as a blend (Divya et al., 2016). PVA/PVP blends have been reported for several uses (Archana et al., 2007; Baraker and Lobo, 2016; Hemalatha et al., 2016).

Generally, solution blending of different polymers is one of the methods used to get new material with a variety of properties. These properties mainly depend on the characteristics of the parent homopolymers and the blend composition (Persano et al., 2006). Hence, study of these systems is receiving increasing attention, since an adequate mixture of the polymers can be used to optimize the performance of polymer-based systems. In this case, whether the nature of the blend is intermediate between the properties of the components or is considerably different, it will be determined by the miscibility and phase behavior of the blend. Miscibility at the molecular level is possible only when the different polymers are capable of establishing specific interactions between their chains.

Use and application of few nanoparticles in reservoir have been studied. During the EOR process, usually saline water is used. Chemical methods are the most common methods, which are used for excessive water control and profile modification. During oil recovery, seawater is used as a base fluid for injecting chemical/materials including nanomaterials, polymer, crosslinker within the reservoir (Zhang et al., 2014). Several nanoparticles are being used for research, among them silica dioxide (SiO_2) is one, which has shown prominent results. The compatibility and strengthening properties of SiO_2 have been studied and reported (Michael et al., 2018; Liu et al., 2017). In recent times, the usage of surfactants with nanoparticles in oil recovery has been gaining vital significance by many researchers. Nanocomposite gel systems for EOR have been considered and resulted in improved thermal stability for heterogeneous reservoirs. Zirconium hydroxide nanoparticles along with gels have been used for water shut-off treatments (Michael et Al., 2018; Liu et al., 2017; Lashari et al., 2018; Jafarnezhad et al., 2016; Adewunmi, 2015).

This chapter consists of the synthesis and characterization of the conventional and nanocomposite hydrogels for enhancing the oil recovery factor from hydrocarbon reservoirs. Synthesized gels were characterized using various techniques like Ultraviolet-visible spectroscopy (UV-Vis), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), etc. The mechanism of bond formation (hydrogen bonding) between polymer and crosslinker and nanoparticle interaction is also well described in this chapter.

3.2 Experimental Procedure

3.2.1 Materials

Polyvinyl alcohol (PVA) with an average molecular weight of 1,04,500 g/mol and hydrolysis degree of 99.0% and polyvinylpyrrolidone (PVP) with molecular weight 44,000 g/mol were provided by Central Drug House Private Limited (India). The crosslinker was prepared using resorcinol which was procured from Fisher Scientific with a purity of 99.0%. Sodium hydroxide and sodium chloride were obtained from Molychem, India. Sodium hydroxide (NaOH) solution was made using water to adjust the pH of the system approximately. Leaves of a plant, *Moringa oleifera* were collected from the fields in Jais, India.

3.2.2 Methods of Gel Preparation

3.2.2.1 Preparation of PVP:RF, PVP/PVA:RF and PVA:RF Blend Gel Systems

Bulk gels or polymer gelant formulations (before being gelled) contain different polymers such as PVA, PVP, etc. Initially, stock solutions of different polymers and crosslinkers were prepared using 0.5% (w/v) brine (NaCl) separately. Crosslinkers and polymer solutions were prepared as follows:

(a) The bulk gel solutions were prepared by mixing 2.0% (w/v) of PVA polymer and 2.0% (w/v) of PVP polymer in 0.5% brine (NaCl). PVA and PVP used for making the solution were found to have 8.0% and 6.0% moisture content respectively. Brookfield viscosity of PVA and PVP was observed and found to be 0.86 cP and 0.67 cP respectively. It was mixed at room temperature and then aged for 24 hours.

(b) 2.0% (w/v) Resorcinol solution was prepared in 0.5% (w/v) brine (NaCl) and 37% formaldehyde (Resorcinol formaldehyde = RF) was used to prepare crosslinker. The resorcinol-formaldehyde solution was prepared at low temperatures to avoid crosslinking, which is possible at high temperatures. The solution of PVA was prepared using a magnetic stirrer with 800 rotation per minute (rpm) at room temperature, while resorcinol solution was prepared at a temperature of 30°C using 800 rpm because it was easily soluble at room temperature.

(c) A stock solution of PVA and PVP polymer was taken separately and was mixed with a pre-defined concentration of crosslinker. After mixing of solution, pH adjustment was done using sodium hydroxide solution to get the desired pH. Finally, after taking the pH of gelant and maintaining it as per requirement, about 25 mL of gel formulations were transferred into scintillation vials (30 mL, Riviera glass Pvt. Ltd.). The crosslinking reaction was started when the gelant formulation was placed in the oven at a preferred temperature of 90°C. The gel strength was expressed according to Sydansk's strength code (Sydansk, 1987). The schematic representation of gel formation is given in **Figure 3.1.**

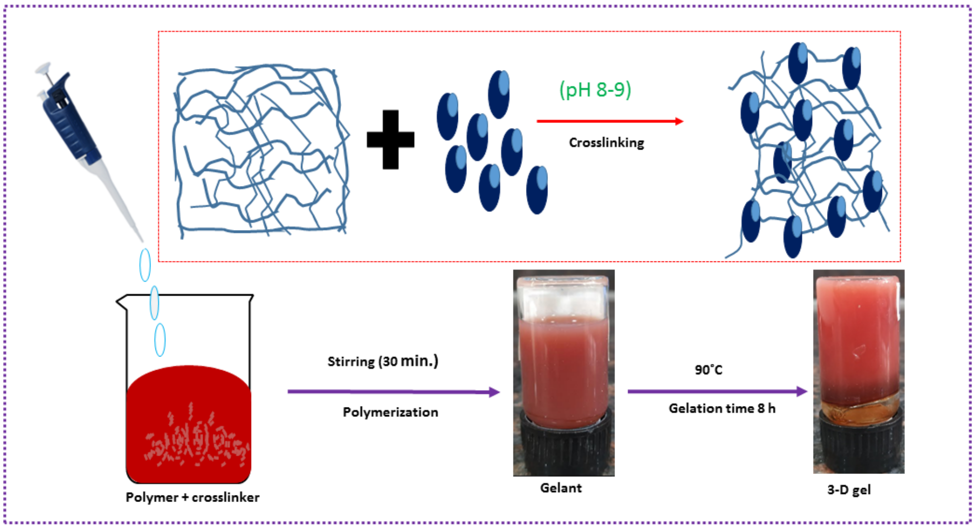

Figure 3.1 Schematic representation of gelation mechanism of gel systems.

3.2.2.2 Synthesis of PVP:RF Conventional and PVP-ZnO:RF Nanocomposite Gels

(a) Synthesis of Plant Extract and Bio-Synthesis of Pure ZnO:

The plant extract was prepared by using leaves of *Moringa oleifera* plant. The leaves were collected from the fields of Jais, India and were properly washed using tap water and then twice using double distilled water. They were then kept in sunlight, dried for 2-3 days and finally crushed into powdered form. Crushed leaves were further used to prepare plant extract by heating 10 gms of leaves powder with 200 mL of distilled water at 100ºC for around 2 hours and then cooled at room temperature. After cooling, the solution was filtered using Whatman filter paper no. 1. The filtrate was then stored at 4℃ in an amber bottle for further experimentation.

15 mL of Leaf extract was added to 35 mL of 200 mm zinc acetate dehydrate (prepared by dissolving 1.536 g of zinc acetate dehydrate in 35 mL of distilled water). The reaction mixture was thoroughly stirred using a magnetic stirrer for about 6 hours. The pH of the solution was adjusted at 12 and the reaction mixture was heated at 90ºC temperature overnight with magnetic stirring. After heating the solution overnight, the white powder, dispersed in solution, was centrifuged at 13,500 rpm for 15 minutes. The obtained powder was washed with distilled water and then using ethanol. It was eventually dried overnight at 90ºC and was crushed into a fine powder using mortar and pestle.

(b) PVP:RF and PVP-ZnO:RF Gel Preparation:

PVP-ZnO:RF (Nanocomposite)gelling solutions containing 2000 ppm and 5000 ppm ZnO were prepared at room temperature. Initially, 1wt% PVP solution was prepared using 1 wt% NaCl. Resorcinol (2 wt% resorcinol)-formaldehyde (RF) was used as a crosslinker (R:F/1:0.1). After mixing of polymer and crosslinker in the brine solution, it was aged for 24 hours at room temperature. The nanocomposite gelling solutions filled with various ZnO amounts were developed by adding a weighed quantity of ZnO (in ppm) into a 20 mL polymer solution. Digital ultrasonic cleaning was immediately performed on the solution of PVP and ZnO for homogenization for 15 minutes. After homogenization, crosslinker was added to the solution and stirred for 30 minutes. The pH of the conventional and nanocomposite gelling solution was maintained at approximately 9. The ratio of polymer (with and without ZnO) and crosslinker solution was 1:0.25 (20 mL and 5 mL respectively). The procedure followed for the preparation of ZnO nanocomposite polymeric gel was reported elsewhere (Michael et al., 2018; Liu et al., 2017). Lastly, the gelant solution with and without ZnO was poured into the ampoules (30 mL) and ampoules were sealed at the neck using Teflon tape. Sealed ampoules were finally kept in an oven at 90ºC temperature. The schematic representation of gel formation is given in **Figure 3.2.**

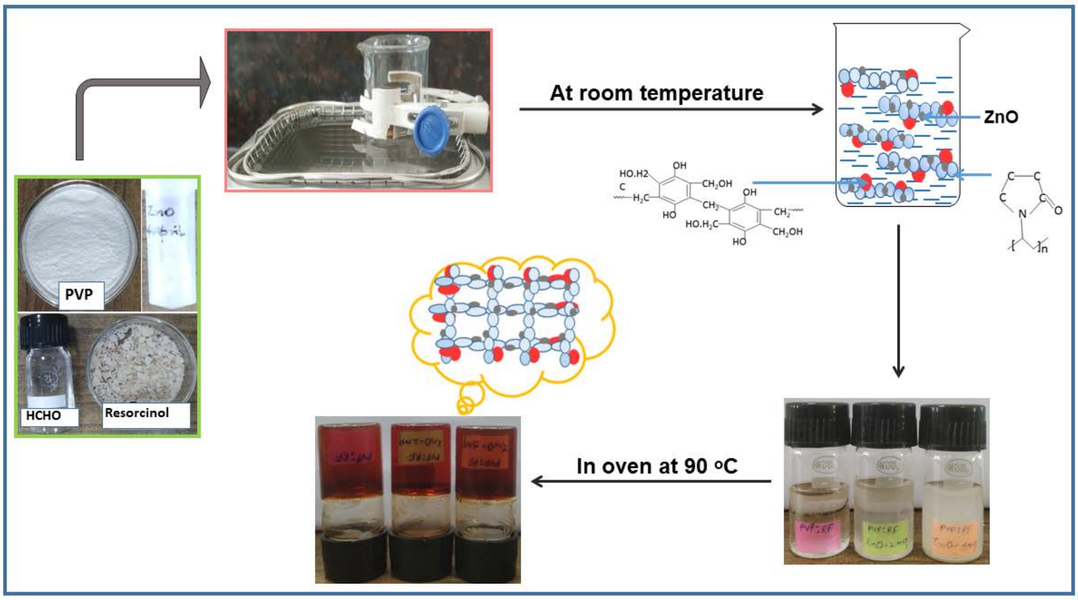

Figure 3.2 Schematic representation of gel formation of conventional (PVP:RF) and nanocomposite (PVP-ZnO:RF) gels.

3.2.2.3 PVA:RF Gel Preparation

Polymeric gelant formulations (before being gelled) contain different concentrations of crosslinker. Initially, stock solutions of polymer and crosslinker were prepared using distilled water. These solutions were prepared as follows:

(a) 2.0% PVA polymer (w/v) in 100 mL solution was mixed and stirred at the rate of 800 rpm for 8 hours and then aged for 24 hours. The base polymer used for making the solution was found to have 8 .0% moisture content . Brookfield viscosity of PVA was observed at 0.86 cP.

(b) 5.0% Resorcinol (w/v) in a 100 mL distilled water for half an hour was stirred at the rate of 600 rpm.

(c) Formaldehyde

After making all stock solutions, crosslinker using resorcinol and formaldehyde was prepared by stirring at 600 rpm using a magnetic stirrer at room temperature for half an hour to produce its homogenous solution. RF solution (1:0.25) was prepared at low temperature to avoid crosslinking, which is possible at high temperatures. A solution of 2.0% PVA (w/v) was prepared in a beaker using a magnetic stirrer at 90°C and 800 rpm while 5.0% resorcinol (w/v) solution was prepared at 30°C and 800 rpm because it was easily soluble at room temperature. Now, the stock solution of PVA polymer was taken in a separate beaker and mixed with different concentrations of crosslinker separately. The gelation mechanism of gel formation is given in **Figure 3.3.**

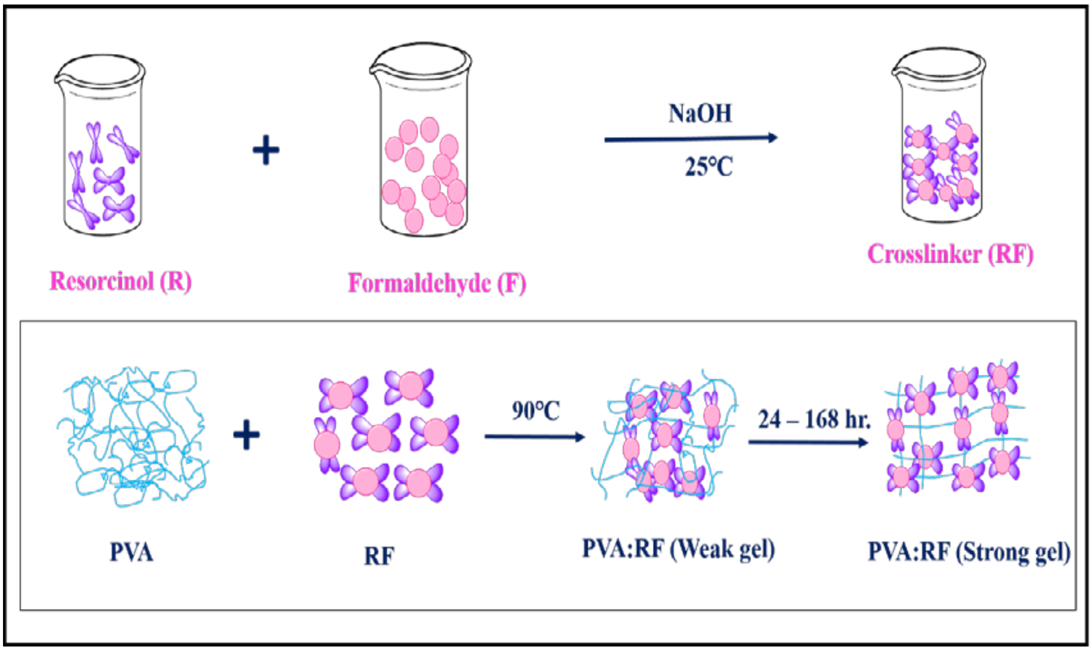

Figure 3.3 Schematic representation of PVA:RF gel formation.

After mixing of solution, pH adjustment was done using sodium hydroxide solution to get the desired pH using Eutech Instruments. Finally, after taking the pH of gelant and maintaining it as per requirement, about 25 mL of gel formulations were transferred into scintillation vials (30 mL, Riviera glass, Pvt. Ltd.). The crosslinking reaction was started when the gelant formulation was placed in the hot air oven at a preferred temperature of 90°C.

3.3 Techniques Used for Characterization of Synthesized Gel Systems

3.3.1 Bulk Gelation Study

Gel strength and gelation time were determined using a breakthrough vacuum method and bottle testing method. For bulk gelation study, samples were poured in scintillation vials and these vials were kept in a preheated oven at a temperature of 90°C. Bulk gelation study was conducted at different polymer concentrations, crosslinker concentrations, salts concentrations and temperatures. Vials were checked using visual observation and viscosity determination at certain time intervals to confirm gel formation and get gelation time.

3.3.2 FTIR Measurements

FTIR spectrometry is a type of absorption spectrometry in the infrared region of the electromagnetic spectrum at which chemical bonds vibrate in either a stretching or bending mode. The tool was used to determine functional groups present in the samples. The spectra of gel samples were recorded in wavenumber range of 250-4000 cm^{-1}.

3.3.3 FESEM Analysis

Field emission scanning electron microscope (FESEM) analysis was conducted to visualize the internal morphological structure of gel samples. FESEM operates in reflection mode to generate an image of the sample surface. This technique utilizes the low energy secondary electrons that are reflected off the sample surface upon the bombardment of the gel samples with a high-energy electron beam. This tool requires a conductive sample surface; therefore, insulating sample surfaces are often coated with a thin layer of a conductive surface.

3.3.4 UV-Vis and XRD Analysis of Nanoparticles

The synthesis of nanoparticles (NPs) and the adsorption study was carried out using Lab India UV-Vis 3200 spectrophotometer. The spectrum was recorded in the range of 300-800 nm with a 10 mm path length quartz cuvette. The purity of the phase was studied by using the PAN analytical X′pertpro MPD diffractometer. X-ray diffraction spectrometry technique helps to investigate the formation and quality of synthesized nanoparticles. Scanning of the samples was done in the range of 2θ from 20 to 80ºC with monochromatic radiation (CuK**α**).

3.3.5 Thermogravimetric Analysis

The thermogravimetric analysis technique was used to detect the response of the nanocomposite gel system and the conventional gel system against rising temperatures. The basic principle of the technique is to raise the temperature of the sample below its melting point, a reduction in the weight of the sample is observed due to the evaporation of water present in gel networks. Thermogravimetric analysis (TGA, Linseis PT 1000) of the synthesized gels was carried out in the nitrogen atmosphere by maintaining the heating rate of 3°C/min from 40 to 120ºC.

3.3.6 DSC Analysis

The differential scanning calorimetry (DSC) profiles of the samples were recorded on a DSC 4000 from Perkin Elmer under N_2 atmosphere (20mL/min). Pre-weighed (~10mg) polymeric blend samples were taken in an aluminum pan for the measurement. The samples were heated from -20 to 200ºC at a rate of 3ºC/minute with sample mass comprised of 10-20 mg in the crucible. An empty sample pan was used as a reference.

3.3.7 Rheological Characterization

Rheological experiments of gel samples were performed for viscosity and moduli (G’ and G”). Rheological investigations are important and deal with the deformation and flow of the sample as a function of shear deformation. In viscoelastic materials, both viscous and elastic properties are present. These properties were evaluated using a cone plate sensing system using a compact rheometer (MCR-52, Anton Paar, Physica, Austria). Shear rate was varied from 1 to 100 s^{-1} to perform viscosity measurements. Moduli for the samples were investigated in the range of 1 to 100 rad/s of frequency sweep (at constant amplitude). All the experiments were conducted at room temperature.

3.3.8 In-situ Gelation Study

Plugging ability of the conventional and nanocomposite gel was determined by the sandpack flooding experiment. These experiments were conducted at a high temperature of 90°C. A high pressure syringe pump (Teledyne ISCO Model 500D) was run at high pressure, which was used for injecting fluids in the core and sandpack. The injecting fluid was kept in the stainless steel cylinder. Diesel oil was used as pushing fluid for injection of fluid in the core and sandpack. The injection rate was kept constant. Change in pressure was recorded from the pressure gauge used in the flow study set up. After the experiment, a change in permeability of the porous media was calculated using the Darcy’s equation.

In this chapter, all the techniques used to characterize the gels, are described in brief.

3.4 Conclusions

- Three polymeric gel systems (PVP:RF, PVA:RF and PVP/PVA:RF) were prepared and screened for water shut-off treatment using bulk gelation studies and sandpack flooding experiments. On increasing salt concentration, gel strength decreases but gelation time increases.
- In conventional and nanocomposite gels, it was seen that on addition of ZnO nanoparticles, gelation time decreases and gel strength increases. At high temperatures, gel strength decreases and at lower temperature, gel strength increases. It may be due to the availability of a more functional group for bonding.
- In PVA:RF gels, a proper combination of polymer and crosslinker not only contributes to a promising gelation mechanism but also improves gel stability. It was observed, on increasing crosslinker concentration, gel strength increases and gelation time decreases.

CHAPTER 4

BULK GELATION STUDY

CHAPTER 4

BULK GELATION STUDY

4.1 Introduction

Chemical treatments are cost-effective methods for water shut-off operations. Chemical treatments include the pumping of gelant solution into the reservoirs. Gelation time and gels strength are two important factors in gel preparation. Gel strength is related to viscosity. Viscosity or gel strength should be below in order to avoid difficulty during the injection of gelant. To avoid premature gelation of gels, gelation time should be long enough. Polymer, crosslinker concentration, temperature, pH and salinity factors affect the gel strength and gelation time of gels (Singh and Mahto, 2016). Gelation time should be long enough for effectively placing of gel within the reservoir. It has been seen that gelation time in reservoirs is longer than tested in the laboratory.

In the present work, gelant solutions were prepared and placed in scintillation vials. After that bottles were placed in the preheated oven at various desired temperatures. The gelation time was decided by visually checking of vials at certain time intervals and determining viscosity (Moghadam et al., 2014). Gel strength was measured using a breakthrough vacuum method. The main objective of the bulk gelation study was to investigate the effect of polymer concentration, crosslinker concentration, temperature, pH and salinity on gel strength and gelation time.

4.2 Experimental Procedure

4.2.1 Determination of Gelation Time and Gel Strength

To study the gelation time of nanocomposite gel and conventional gels, the bottle testing method was used. This method is referred to as a semi-quantitative and inexpensive method. The gelant solutions were visually checked after a certain time at a temperature of 90ºC. The gel strength of gel systems can be controlled by varying the concentration of different components. The gel strength was determined by the breakthrough vacuum method (Zhao et al., 2013). The schematic diagram of the used experimental setup has been illustrated in **Figure 4.1** and Sydansk strength code was used to decide the strength of prepared gel samples (Sydansk, 1987). It is depicted in **Figure 4.2** and in **Table 4.1.**

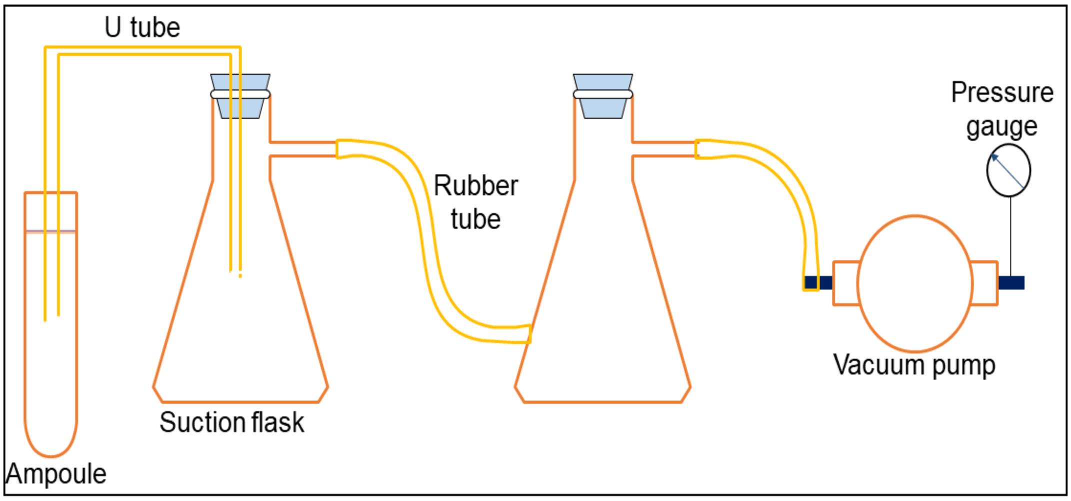

Figure 4.1 Schematic diagram of the breakthrough vacuum method.

Table 4.1 Sydansk gel strength code

Code	Gel type	Gel behavior in bottle
A	No detectable gel	The gel solution appears to have almost the same viscosity as an initial solution.
B	Highly flowing gel	The gel is comparatively more viscous.
C	Flowing gel	The gel flows up to the cap upon inversion.
D	Moderately flowing gel	A small portion of gel does not flow upon inversion.
E	Barely flowing gel	A small portion of gel slowly flows upon inversion.
F	Highly deformable non-flowing gel	No gel flow upon inversion.
G	Moderately deformable non-flowing gel	The gel flows approximately halfway upon inversion.
H	Slightly deformable nonflowing gel	No gel surface deformation upon inversion.
I	Rigid gel	No gel surface deformation on inversion.
J	Ringing rigid gel	Strong gel upon inversion.

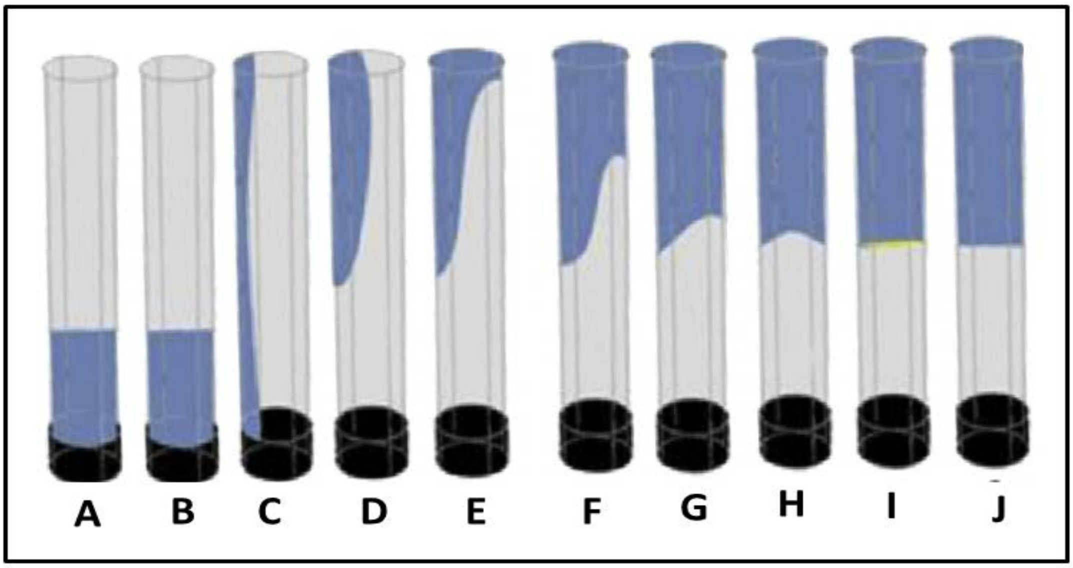

Figure 4.2 Free flowing gel to ringing rigid gel (Karimi et al., 2014).

4.3 Results and Discussion

4.3.1 Bulk Gelation Study of PVP:RF, PVA:RF and PVP/PVA:RF Gels

4.3.1.1 Gelation Time and Gel Strength

Gelation time and gel strength are two key factors for gel placement and plugging ability in the reservoir for any kind of gel. The gelation time should be sufficient to place the gel into the targeted zones of the reservoir (Karimi et al., 2014). To observe the gelation time, the gel solutions of different concentrations of polymer, crosslinker and salinity were prepared. The prepared samples were placed into ampoules and put in the pre-heated oven at a temperature of 90°C. These ampoules were observed after every 1 hour to determine the gelation time and gel strength of the samples. Polymer or blend and crosslinker ratio were fixed in the ratio 1:0.25 for all samples.

4.3.1.2 Effect of Salinity on Gel Time

One of the main influencing factors on the gel is the presence of salt in the reservoir. The salinity effect was checked using NaCl and $CaCl_2$ (5000-25000 ppm) at 90ºC. With the increase of the concentration of the monovalent ion (sodium), it is assumed that sodium is assembled around the functional groups of the polymers. Due to the presence of both anions and cations, double layer formation takes place around the functional group of the polymers. This generated double layer causes the shrinkage of the polymer chains. The presence of divalent ion (calcium) has negative effects on the gel strength. Divalent ion may even cause the polymer to be deposited. But the presence of these divalent ions leads to gelation time increment (Bai et al., 2015).

The effect of inorganic salts (NaCl and $CaCl_2$) on the gel strength and gelation time of gels is shown in **Figures 4.3a and 4.3b**.

In 5000 ppm NaCl salt solution, gel strengths for PVP:RF, PVP/PVA:RF and PVA:RF gel systems were observed to be 25000, 16000, and 12000 Pa respectively. In 25000 ppm NaCl salt solution, found gel strengths were 11, 9 and 7 kPa respectively. In 5000 ppm $CaCl_2$ salt solution, gel strengths for PVP:RF, PVP/PVA:RF and PVA:RF gel systems were observed 23000, 14000 and 11000 Pa respectively. In 25000 ppm $CaCl_2$ salt solution, gel strengths were found to be 8, 6 and 6 kPa respectively. The very low gel strength of PVA:RF gel system was due to crystallinity (Nawar and Petch, 1987; Noguchi and Yang, 1964). It may be due to the precipitation in the presence of NaCl and $CaCl_2$. Therefore, the strength of PVA:RF gel system is highly affected by NaCl and $CaCl_2$ ions.

The gel strength of fresh and effluent gel samples is shown in **Figure 4.4.** Results show that the PVP:RF gel system has a higher gel strength in comparison to PVP/PVA:RF and PVA:RF gel systems.

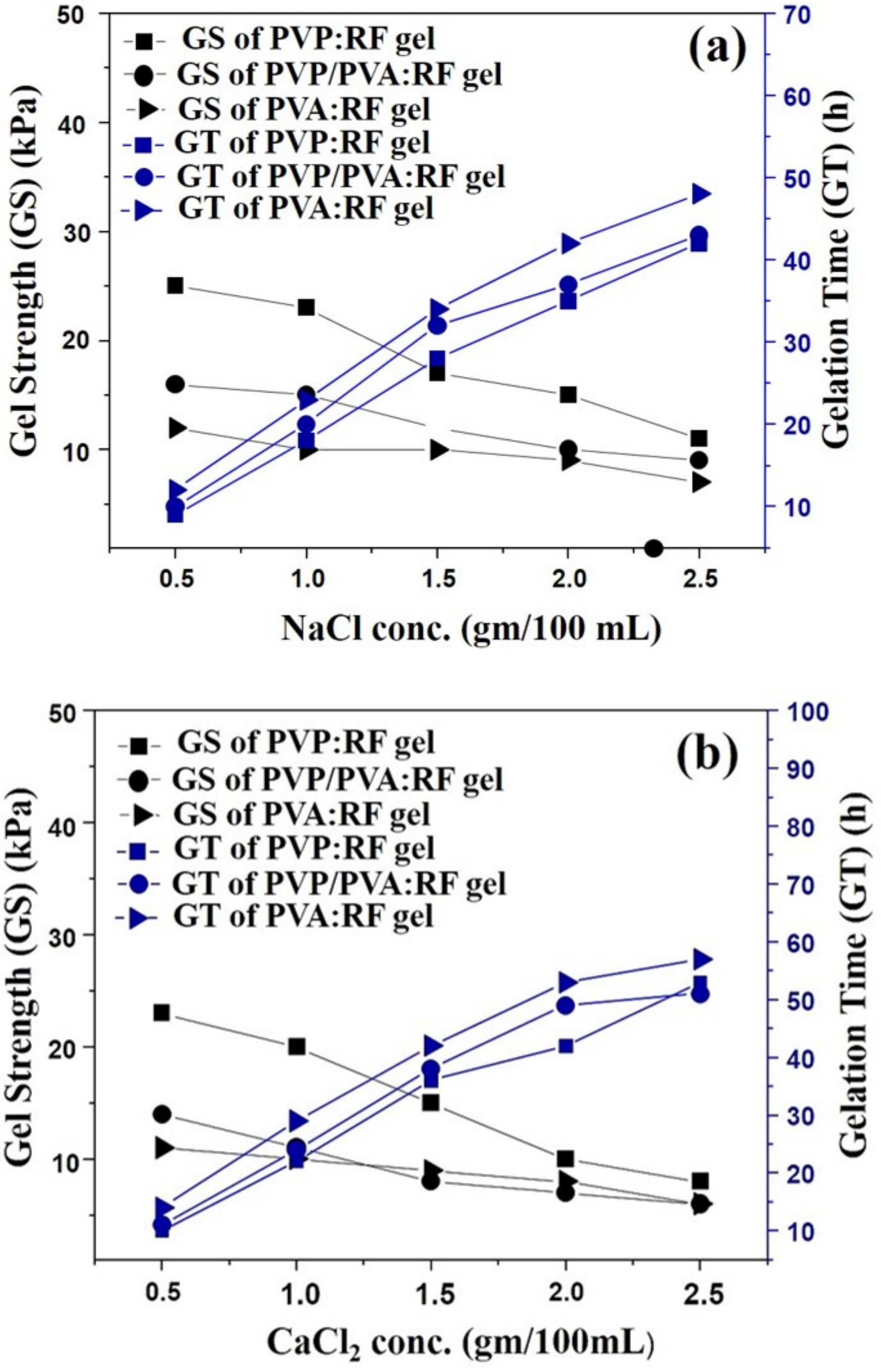

Figure 4.3 Effect of different concentrations of (a) NaCl and (b) CaCl$_2$ on the PVP:RF, PVP/PVA:RF and PVA:RF gel systems.

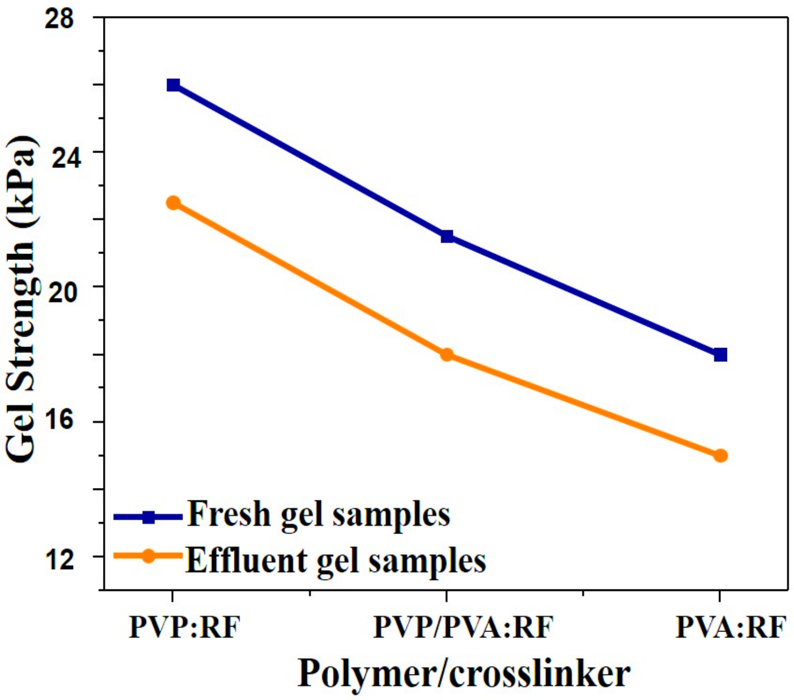

Figure 4.4 Gel strengths of the fresh and effluent gel samples.

4.3.2 Bulk Gelation Study of PVP:RF and PVP-ZnO:RF Gel Systems

4.3.2.1 Effect of Polymer Concentration

Polymer concentration for making the gel is critical and should always obtain the minimum polymer concentration for preparing gel solution. The effect of polymer concentration can be observed as a Sydansk gel strength code. It is a cheap and fast method. The formation of the gel is determined by the codes between A to J. The code of A to J indicates gel nature from free flowing to hard ringing rigid gel (Sydansk, 1990). PVP-ZnO:RF (5000 ppm) gel sample with different polymer concentrations (0.5 – 3 wt%) was used. With the study of conducted experiments at 90ºC, it is observed that the increase of PVP polymer concentration decreases the gelation time and increases the gel strength. It is depicted in **Figure 4.5.**

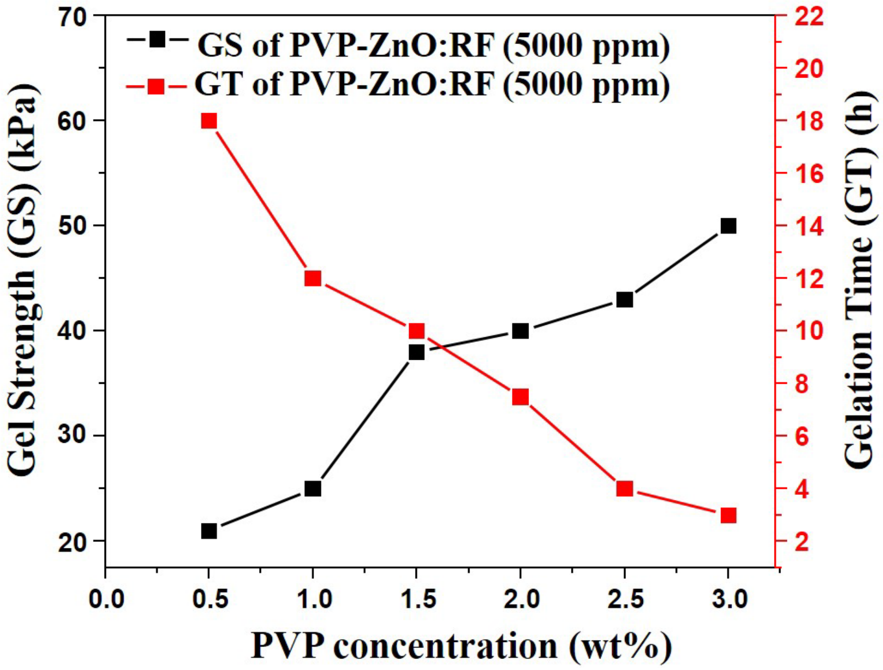

Figure 4.5 Effect of polymer concentration on gel strength and gelation time at 90ºC.

4.3.2.2 Effect of Crosslinker Concentration

Crosslinker causes the bond between polymer chains and increases the strength of gel (Yadav and Mahto, 2014). Resorcinol is completely soluble in water and with formaldehyde, it is used as crosslinker. A high concentration of crosslinker leads to a decrease in gelation time and an increase in gel strength. PVP-ZnO:RF (5000 ppm) gel sample with different crosslinker concentrations (0.5- 3.0%) was characterized at 90ºC. On increasing more concentration than 3.0% (w/v) of crosslinker, crosslinking causes the polymer molecules to get closer to each other and then the gel shrinks. This causes the gel strength weaker thus the syneresis has occurred. It is depicted in **Figure 4.6.**

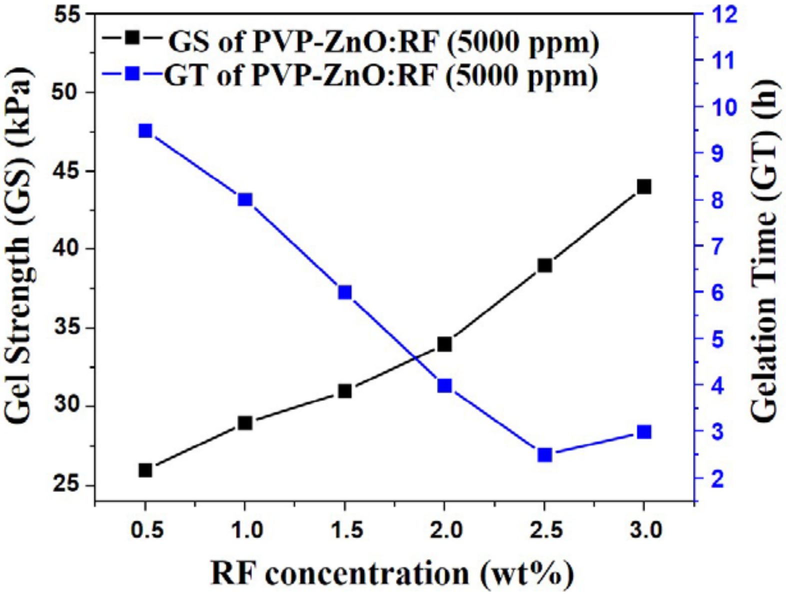

Figure 4.6 Effect of crosslinker concentration on gel strength and gelation time at 90ºC.

4.3.2.3 Effect of Salinity

One of the main influencing factors on the gel is the presence of salt in the reservoir. The salinity effect was checked with NaCl and $CaCl_2$ (0.25 – 1.0%) at 90ºC. With the increase of the concentration of the single ion (sodium), it is assembled around the carbonyl group of polyvinyl pyrrolidone. Due to the presence of both anions and cations, double layer formation takes place. This generated double layer causes the shrinkage of the polymer chains. The presence of divalent cation (calcium) has negative effects on the gel strength. The divalent cation may even cause the polymer to be deposited. But the presence of divalent cation leads to gelation time increment (Bai et al., 2015). NaCl and $CaCl_2$ effect on conventional and nanocomposite gel systems is depicted in **Figures 4.7 and 4.8.**

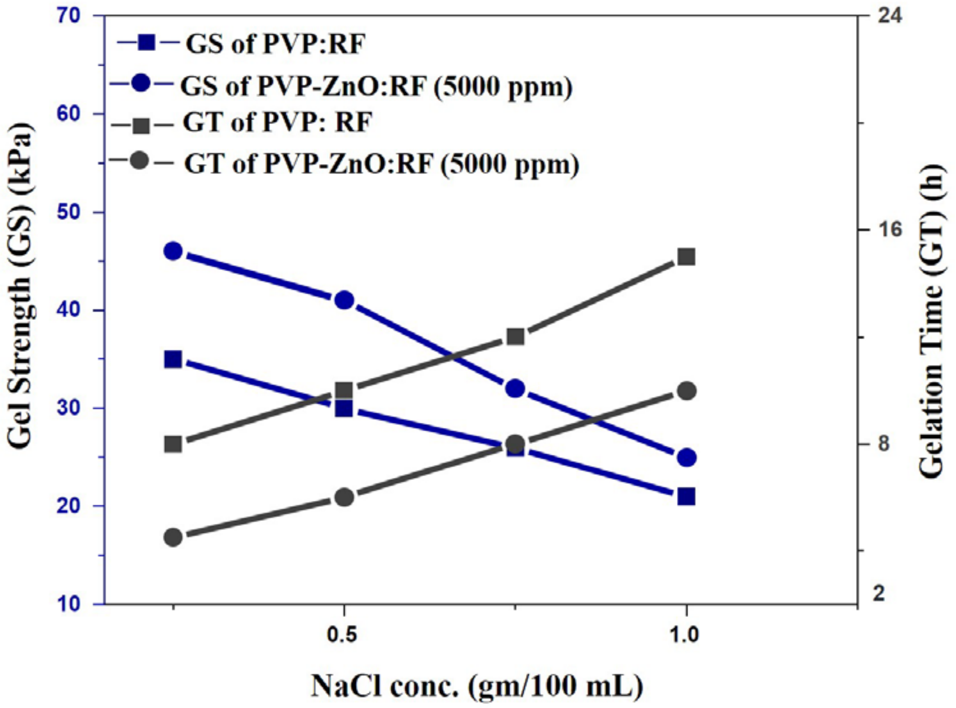

Figure 4.7 Effect of NaCl salt on gel strength and gelation time at 90ºC.

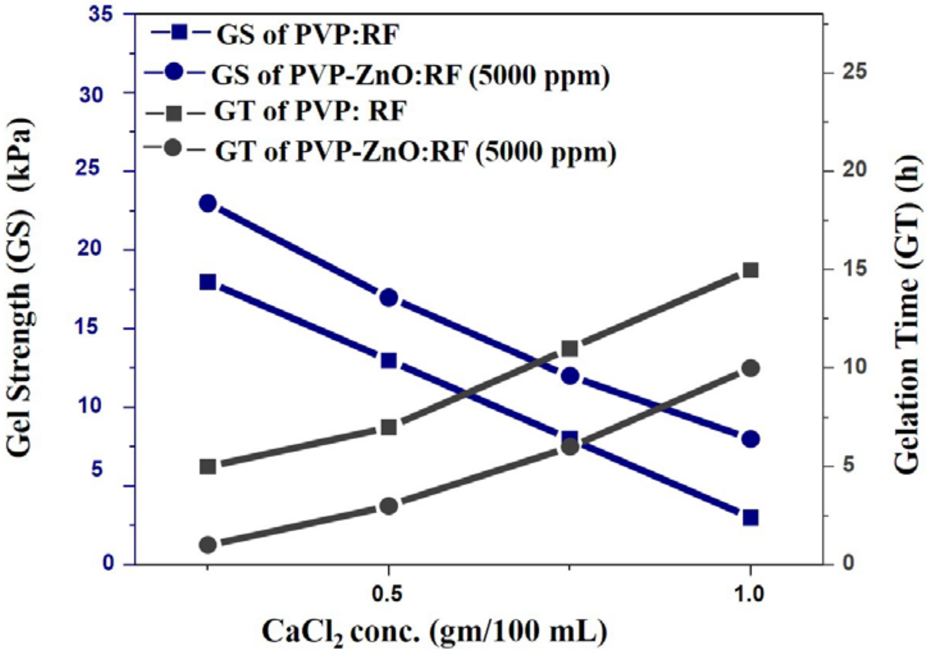

Figure 4.8 Effect of $CaCl_2$ salt on gel strength and gelation time at 90ºC.

4.3.2.4 Effect of Temperature

Gelation temperature plays a very important role in gel formation and its thermal stability. The increment in temperature decreases the gelation time. Conventional gel (PVP:RF) and nanocomposite gel PVP-ZnO:RF (5000 ppm) were investigated from 50-90ºC. **Figure 4.9** demonstrates that gelation decreased with an increase in temperature. Gelling time for the conventional gel system was noted to be 22 hours at 50ºC, whereas the gelling time of nanocomposite gel was 18 hours at the same temperature. Gelling time sharply decreased to 10 hours and 8 hours at 90ºC for PVP:RF and PVP-ZnO:RF gel respectively. The results indicated that temperature accelerates the thermal interactions between polymer molecules and crosslinker. Due to the interaction between polymer and crosslinker molecules, inner particle forces also increase, therefore, gel strength also increases at high temperatures. At 50ºC, gel strength was 22.5 kPa and 25 kPa and at 90ºC, it was 26 kPa and 29 kPa for PVP:RF and PVP-ZnO:RF gel system respectively. Result also indicates that nanocomposite gel has good gel strength but less gelation time than conventional gel.

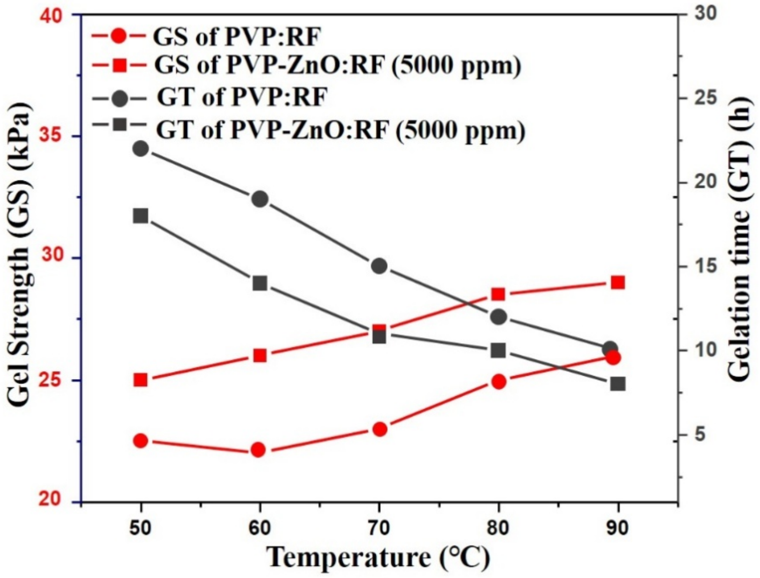

Figure 4.9 Effect of temperature on gel strength and gelation time.

The gelation time was also correlated to the temperature according to the Arrhenius equation:

$$K = K_0 e^{\frac{-E_a}{RT}} \qquad \text{..... (iv)}$$

Where, k is the reaction rate constant, K_0 is frequency factor, E_a, the activation energy (KJ/mol), R, the gas constant (KJ/mol.K) and T is the absolute temperature (K). Equation (iv) was modified by introducing the gelation time (GT) instead of the reaction rate constant K and M as the frequency factor.

$$\mathrm{GT} = \mathrm{M}e^{\frac{\mathrm{E_a}}{\mathrm{RT}}} \qquad \text{..... (v)}$$

Where, GT is gelation time (h) and M is the rate constant (h). Equation (v) can be modified as follows:

$$\ln GT = \frac{E_a}{RT} + \ln M \qquad \text{..... (vi)}$$

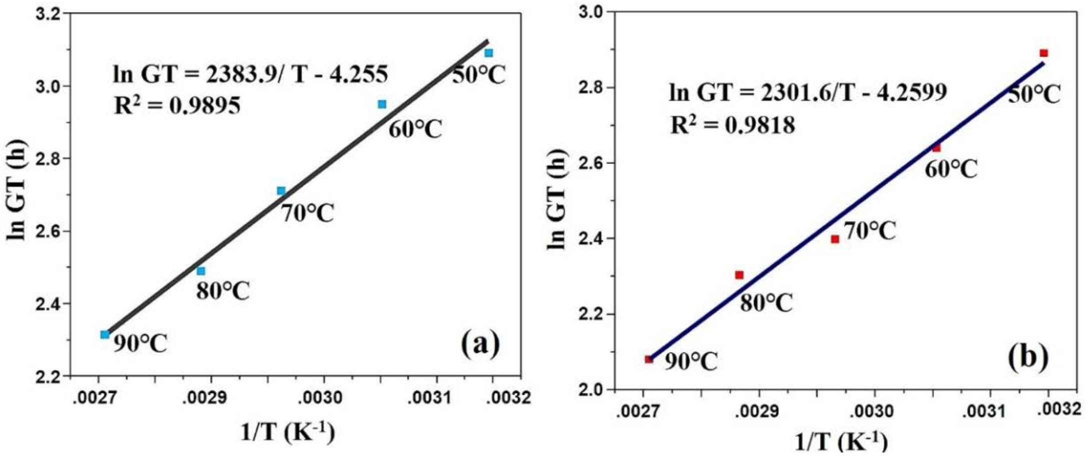

Figure 4.10 Arrhenius type graph of (a) PVP:RF and (b) PVP-ZnO:RF (5000 ppm).

As we can see from equation (vi), there is a linear relationship between ln GT and the inverse of temperature (1/T) (Singh et al., 2018). It is depicted in **Figure 4.10**. Calculated from the slope of **Figure 4.10**, the activation energy was 19.786 and 19.098 KJ/mol for PVP:RF and PVP-ZnO:RF (5000 ppm) gel systems respectively.

4.3.3 Gelation Time and Gel Strength Measurement of PVA:RF Gel Systems

Gelation time and gel strength are two key factors for gel placement and plugging ability in the reservoir for any kind of gel. The gelation time should be sufficient to place the gel into the targeted zones of the reservoir. To observe the gelation time, the gel solutions of different concentration of crosslinker with a fixed concentration of polymer were prepared. Gel strength and gelation time for different Polymer/crosslinker ratio are shown in **Figure 4.11.**

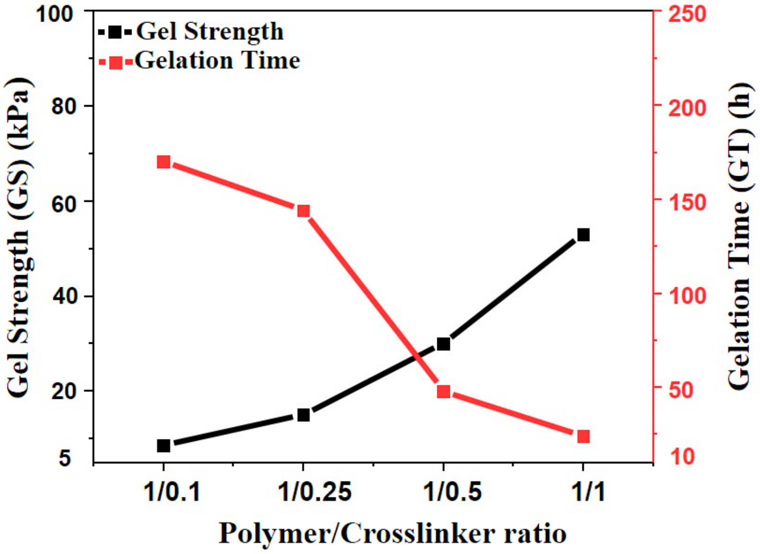

Figure 4.11 Effect of polymer/crosslinker ratio on gel strength and gelation time at 90°C.

The prepared samples were injected into ampoules and put in the preheated oven at 90°C. These ampoules were observed after every 1 hour to determine the gelation time and gel strength of the samples. The gel strength can be controlled from the gelation code A to J by varying the concentration of polymer and crosslinker. The gel strength was highly stable for the polymer/crosslinker ratio 1/1 i.e., 53 kPa and low for 1/0.1 i.e. 8.6 kPa and gelation time was vice versa. It can be shown from the result that gelation time decreased with the increase in the concentration of crosslinker (Yadav and Mahto, 2014).

4.4 Conclusions

- In PVP:RF, PVP/PVA:RF and PVA:RF gels, it was observed that on increasing salt concentration, gel time increases.
- In PVP:RF conventional and PVP-ZnO:RF nanocomposite gels, later one has a better gel strength.

- In PVP:RF conventional and PVP-ZnO:RF nanocomposite gels, on increasing temperature, gelation time decreases and gel strength increases.
- In PVA:RF gels, on increasing polymer or crosslinker concentration, gel strength increases.

CHAPTER 5

HYDROGEN BONDING, UV-VIS, XRD, FTIR AND FESEM ANALYSIS

CHAPTER 5

HYDROGEN BONDING, UV-VIS, XRD, FTIR AND FESEM ANALYSIS

5.1 Introduction

The reaction mechanism is basically a microscopic path in which reactants are transformed into new products. The reaction may involve the interaction between functional groups of polymer and crosslinker. The reaction mechanism tells about the reaction between polymer and crosslinker (Nam et al., 2019). In our synthesized gels, the reaction takes place between carbonyl and alcoholic groups. The Fourier transform infrared spectroscopy states about the absorption of infrared radiation by the sample versus wavelength. Change in the wavenumber expresses about the formation of the product as an increase or decrease in wavelength (Mansur et al., 2008). Field emission scanning electron microscopic technique works with electrons instead of light. These electrons are liberated by a field emission source (Cascone et al., 2004). The sample is scanned by electrons in a zig-zag pattern. UV-Vis spectroscopy is used for the quantitative determination of analysts such as organic compounds, nanocomposite, etc. A UV-Vis beam is passed through a cuvette with a wavelength varying from 180-1100 nm. X-ray diffraction tool is used to identify and characterize unknown crystalline materials (Timaeva et al., 2020). Analysis of ZnO nanoparticles was done using this technique.

5.2 Techniques

5.2.1 Fourier Transform Infrared Spectroscopy (FTIR) Measurements

The Fourier transform infrared spectra of the samples were recorded by taking solid dried powder of gel samples. The Perkin Elmer Spectrum PIKE MIRacle single reflection horizontal attenuated total reflectance (ATR) accessory equipped with a ZnSe. ATR Crystal was used for recording the spectra. FTIR spectrum is obtained from performing a mathematical Fourier transform on the interferogram. FTIR spectrometry is a type of absorption spectrometry in the infrared region of the electromagnetic spectrum at which chemical bonds vibrate in either a stretching or bending mode. The tool is used to determine functional groups present in the samples. The spectra of prepared gel samples were recorded in the wavenumber range of 250-4000 cm^{-1}.

5.2.2 Surface Morphological Analysis by Field Emission Scanning Electron Microscopy (FESEM)

Field emission scanning electron microscopic analysis was conducted to visualize the internal morphological structure of gel samples. FESEM operates in reflection mode to generate an image of the sample surface. This technique utilizes the low energy secondary electrons that are reflected off the sample surface upon the bombardment of the gel samples with a high-energy electron beam. It requires a conductive sample surface; therefore, insulating sample surfaces are often coated with a thin layer of a conductive surface. Gold coating for 105 seconds was used for the samples. In general, scanning electron microscopy (SEM) resolution varies from 0.5µm to 20µm. The morphologies of samples were imaged by using FE-SEM Zeiss Supra 40 (accelerating voltage ranged 15 kV).

5.3 Hydrogen Bonding of Different Gel Systems

5.3.1 Hydrogen Bonding in the Mixture of PVP:RF and PVP-ZnO:RF Gels

Crosslinker (Resorcinol-formaldehyde) formation reaction was adapted from Gaca et al., 2013 and 2017. Usually, crosslinkers are used as bridging agents that would bind polymer chains. **Figure 5.1** shows the chemical reaction between resorcinol-formaldehyde. The condensation reaction of crosslinker is given in **Figure 5.2** (Al-Muhtaseb and Ritter, 2003; Gupta and Kandasubramanian, 2015; Kakunuri and Sharma**,** 2018; Prostredny et al., 2019**)**. Hydrogen bonding between PVP polymer and RF crosslinker can be seen from the FTIR graph (Taohong et al., 2017). ZnO reacts with the phenyl –OH group (Kashif et al., 2014; Michael et al., 2018). The interaction between the nanofiller (ZnO) and PVP:RF gel was investigated using the FTIR graph. It is given in **Figure 5.3.** Structure of PVP-Zn is given in **Figure 5.4.**

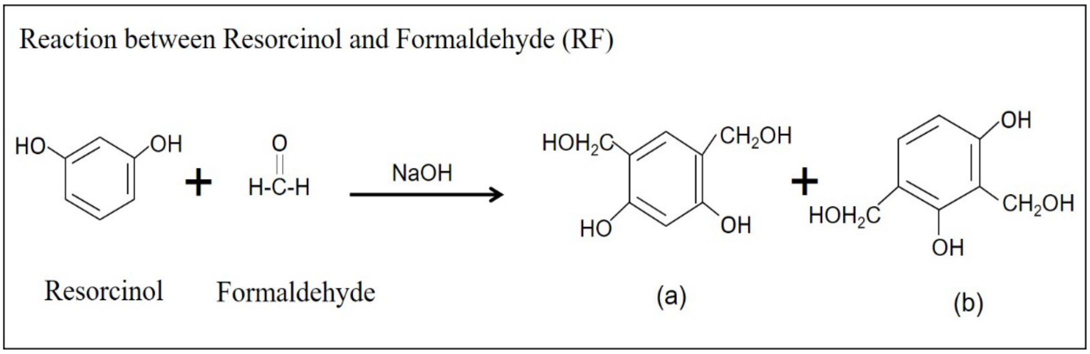

Figure 5.1 Reaction between resorcinol and formaldehyde (RF).

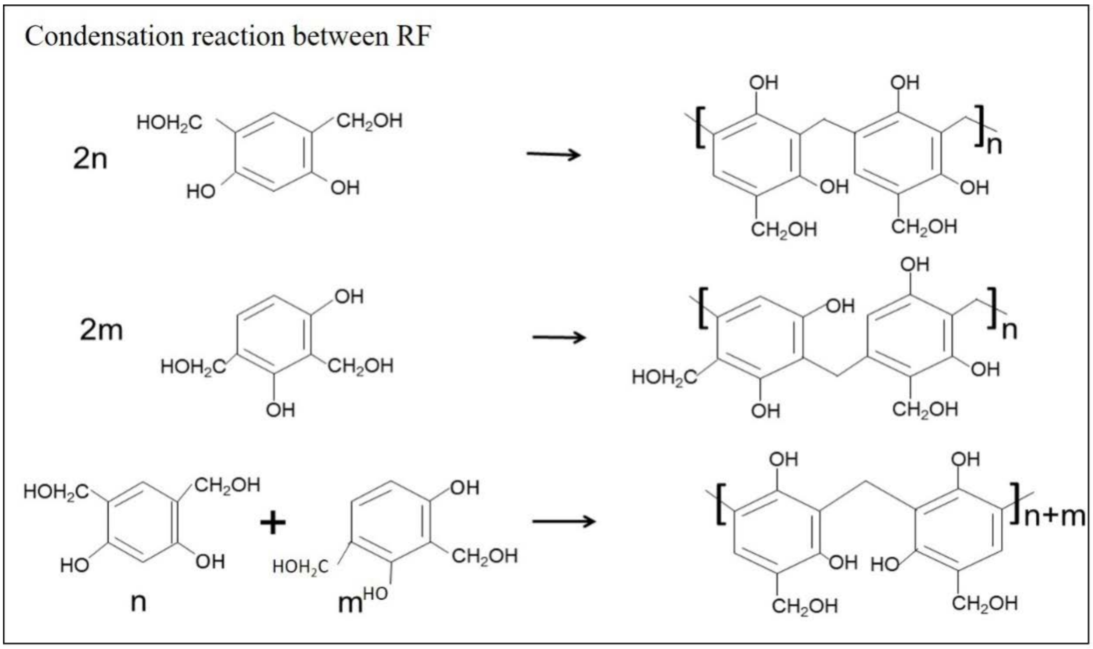

Figure 5.2 Condensation reaction of RF polymer.

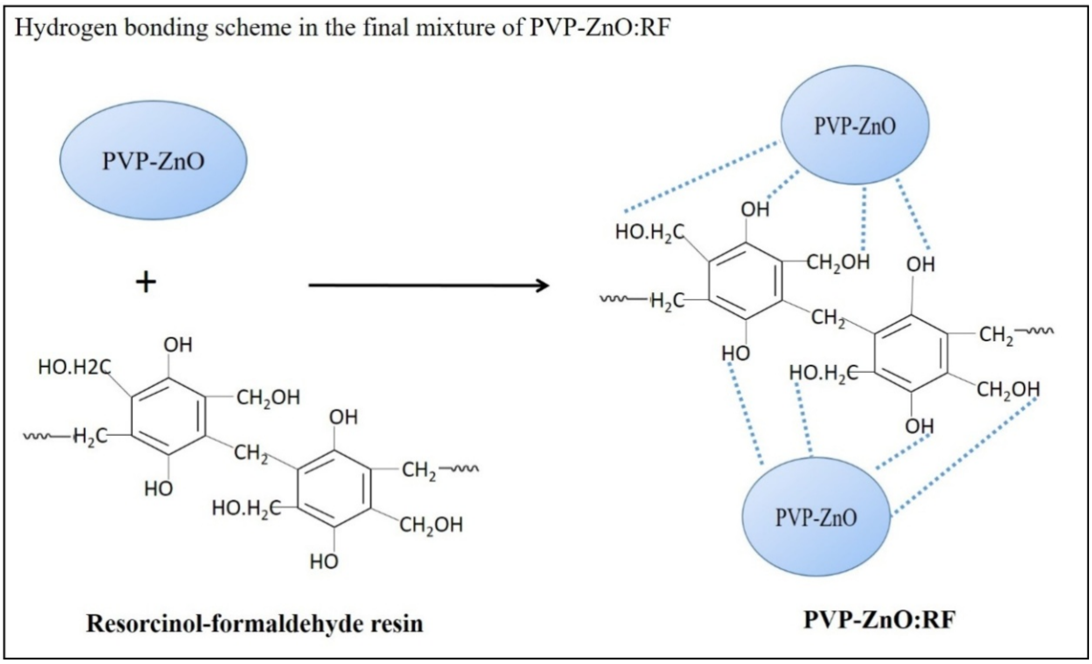

Figure 5.3 Hydrogen bonding and ZnO interaction with PVP:RF.

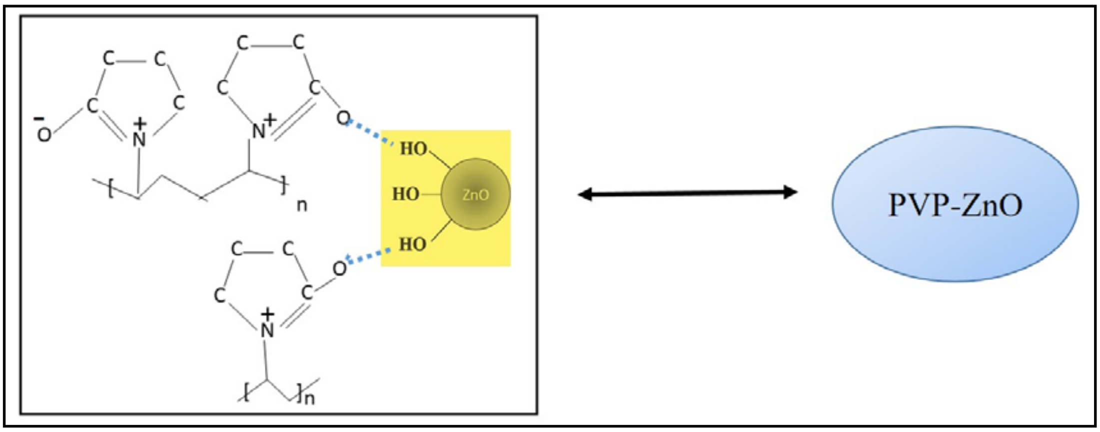

Figure 5.4 Structure of PVP-Zn.

5.3.2 Hydrogen Bonding in the Mixture of PVA:RF Crosslinked Gel

PVA-resorcinol-formaldehyde solutions were prepared with distilled water as described in the materials and methods section. pH was adjusted for different concentrations of gelant formulation to increase the gelation time and lower the corrosion rate while injecting the formulation into the well. The reaction mechanism of the prepared gel is as shown in **Figure 5.5** (Shiao Wei Huo, 2018).

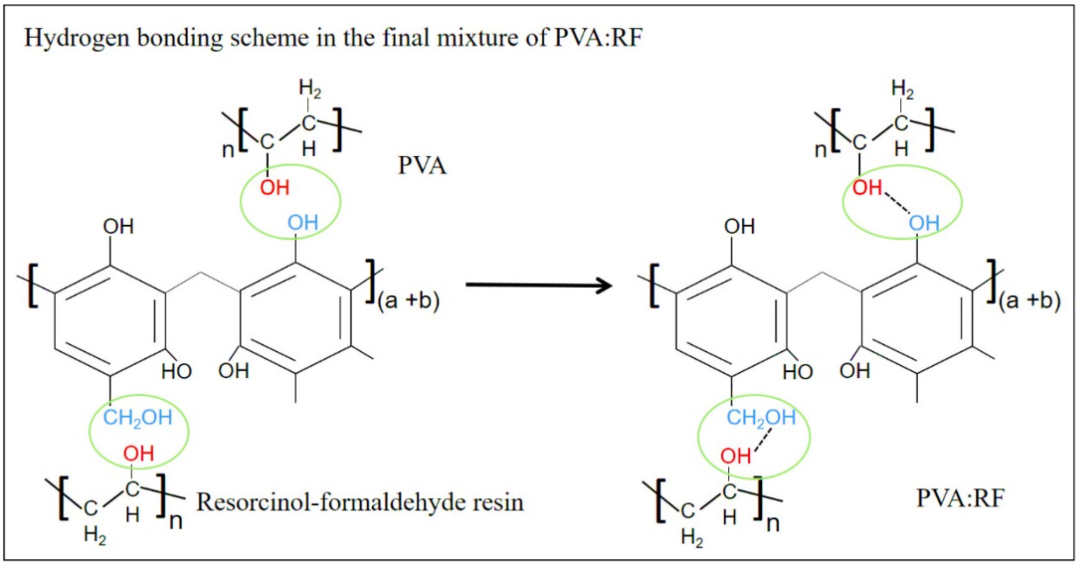

Figure 5.5 Hydrogen bonding of crosslinking reaction between PVA:RF gel.

5.4 Results and Discussion

5.4.1 UV-Vis Spectra and XRD Analysis of ZnO

The UV-Vis spectrum of synthesized nanoparticles reveals a characteristic absorption peak of ZnO nanoparticles at a wavelength of 358 nm. It is depicted in **Figure 5.6.** XRD data of synthesized nanoparticle reveals a series of characteristic peaks with 2θ values of 31.77457º, 34.42689º, 36.27826º, 47.59656º, 56.64333º, 62.93273º and 68.02726º. These peaks were indexed to (100), (002), (102), (110), (103) planes of ZnO hexagonal phase structure respectively. The peaks and obtained Miller Indices are related to the standard hexagonal Wurtzite crystal structure. The data is in accordance with the standard JCPDS card 36-1451. The data not only confirms the synthesis of ZnO nanoparticles but also the absence of other impurities. It is shown in **Figure 5.7**. The average size of the synthesized pure ZnO was calculated using Debye Scherrer's equation, which states

$$D = \frac{K\mathrm{D}}{B\,\mathrm{Cos}\,\theta} \qquad \text{..... (vii)}$$

Where, D is the mean size of the particles; K, a constant having value 0.9; λ, X-ray wavelength; B, the full width at half maximum in radians; and θ, the Bragg diffraction angle in radian.

The average particle size of the ZnO was found to be 10 nm.

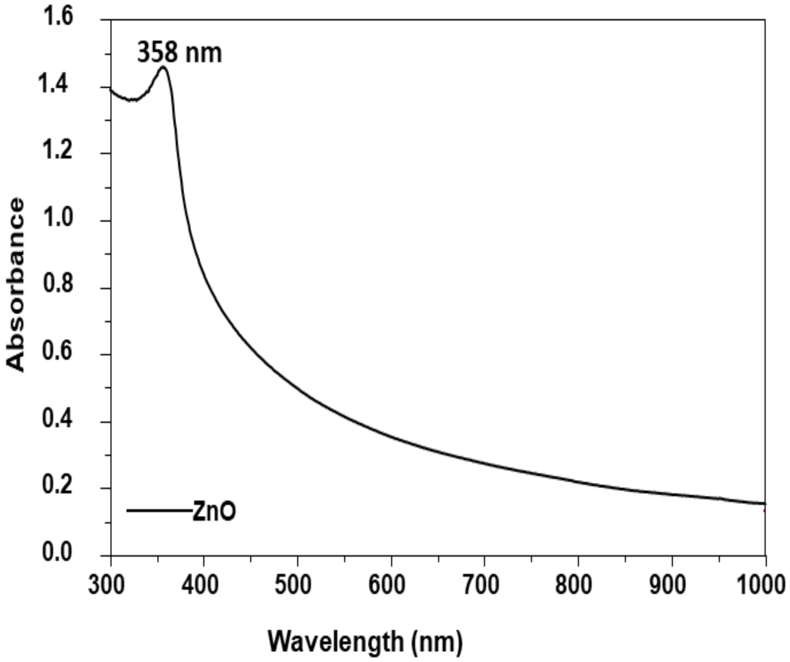

Figure 5.6 UV-Vis spectra of pure ZnO.

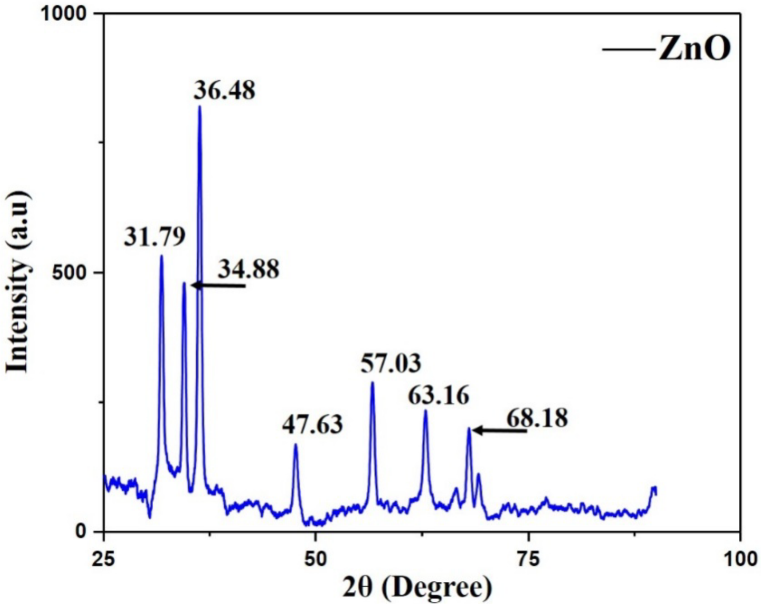

Figure 5.7 XRD spectra of pure ZnO nanoparticles.

5.4.2 Characterization of Gel Systems

5.4.2.1 FTIR Analysis of PVP:RF, PVP/PVA:RF and PVA:RF Gel Systems

Functional groups of the polymeric gel systems and their chemical compositions could be checked using FTIR spectroscopy. Infrared spectra of these materials differ conferring to their composition and may be able to indicate their occurrence of complexation and interaction among various constituents. The FTIR spectra for pure PVA:RF, PVP/PVA:RF and PVP:RF gel samples are shown in **Figure 5.8.** The mutual interaction between them produces modifications in their vibrational mode of the atoms or molecules in the sample, which leads to a change in the physical and chemical properties of the constituents of the complex. The spectrum exhibits bands characteristics of stretching bending vibrations of O-H, C-H, C=O and CH_2.

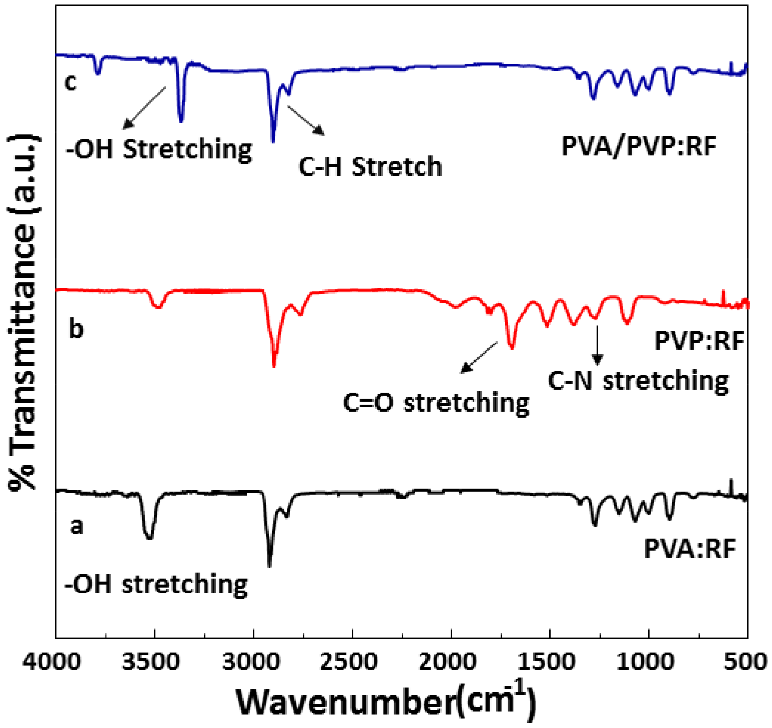

Figure 5.8 FTIR spectra of PVP:RF, PVP/PVA:RF and PVA:RF.

A strong band observed at 3500 cm^{-1} has been assigned to bending mode vibration corresponding to the free –OH group. While another strong band observed around 1660 cm^{-1} described the stretching vibration of C=O attributed to PVP. The band corresponding to CH_2 asymmetric stretching vibration occurs at about 2977 and 2968 cm^{-1}. The peaks of –OH groups due to hydrogen bonding are attributed to 3265, 3285 and 3269 cm^{-1}. A C-C stretching mode is observed at 946 cm^{-1}. A characteristic alcohol band at 1152 cm^{-1} was assigned to the stretching of C-O of PVA, which is affected by hydrogen bonding along with C-H and O-H bending. The band observed at 1390 cm^{-1} has been attributed to combination frequencies of -CH and –OH groups. Characteristics C-N stretching vibration of PVP was observed at 1256 cm^{-1}.

5.4.2.2 FTIR Analysis of PVP:RF and PVP-ZnO:RF Gels

To confirm the chemical functionalities for inducing hydrogen bonding, FTIR spectral analysis was carried out on the PVP:RF with and without ZnO. As shown in **Figure 5.9**, PVP:RF and PVP-ZnO:RF, have characteristic peaks of -(C-N) 1284 cm^{-1}, (C=O) 1639 cm^{-1}, -(C-H) 3060 cm^{-1} and -(O-H) 3321 cm^{-1} due to hydrogen bonding of PVP with RF. In PVP-ZnO:RF, a strong absorption peak was observed at 2342 cm^{-1}. This peak is assigned to be an asymmetrical stretch frequency of - (O-C=O) (as an impurity) (Haling and McCluskey, 2005). The origin of the band at 642 cm^{-1} is due to the metal-oxygen bond, which confirms the synthesis of ZnO (Kumar et al., 2013).

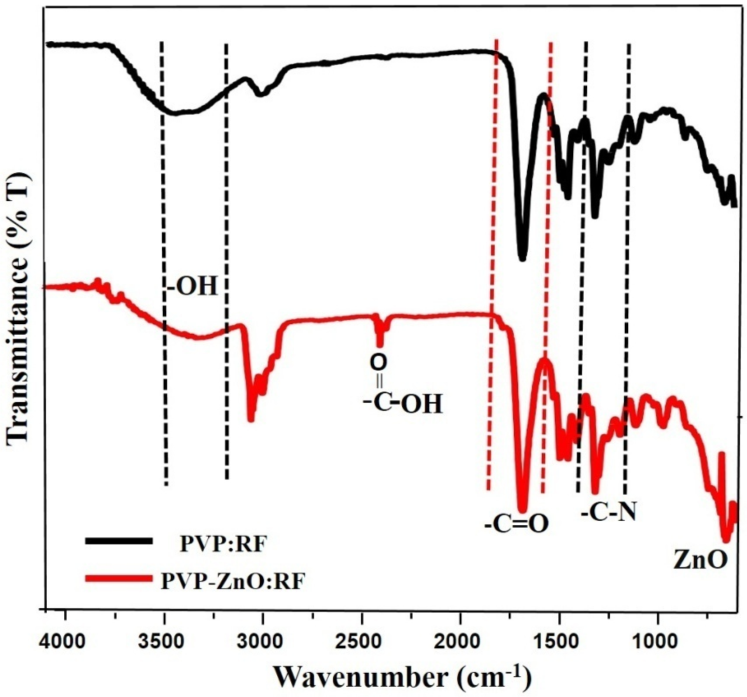

Figure 5.9 FTIR spectrum of PVP:RF and PVP-ZnO:RF.

5.4.2.3 FTIR Analysis of PVA:RF Gels

FTIR spectrum of the gel samples were acquired in the range of 500-4000 cm^{-1}. Infrared spectra of gels show the occurrence of complexation and interaction between various constituents. The mutual interaction between the functional groups produces a change in their vibrational modes of the atoms or the molecules in the gel sample. The FTIR spectra of PVA:RF with different concentrations of crosslinker (RF) is given in Figure 5.10. The spectrum exhibits bands characteristics of stretching and bending vibrations of O-H, C-H, C=C, C-O-H groups. In **Figure 5.10**, a strong band observed at 1087 and 1024 cm^{-1} has been assigned to C-OH bending mode corresponding to aliphatic alcohol. A band observed at 1250 cm^{-1} has been attributed to the C-H bending of the methyl group. The FTIR absorption bands, that appeared at 1285 cm^{-1} range, are attributed to the C-OH stretching frequency of the aromatic alcohol. A band observed at 1473 cm^{-1} is attributed to C-H bending of CH_2

saturated scissoring. Another band found at 1711 and 1635 cm^{-1} indicates a C=C stretching mode. A band detected at 2939 cm^{-1} attributed to the asymmetric stretching mode of the CH_2 group. Absorbance at 3349 and 3311 cm^{-1} corresponds to an O-H group, which could be explained on the basis of intermolecular hydrogen bonding with the adjacent –OH group.

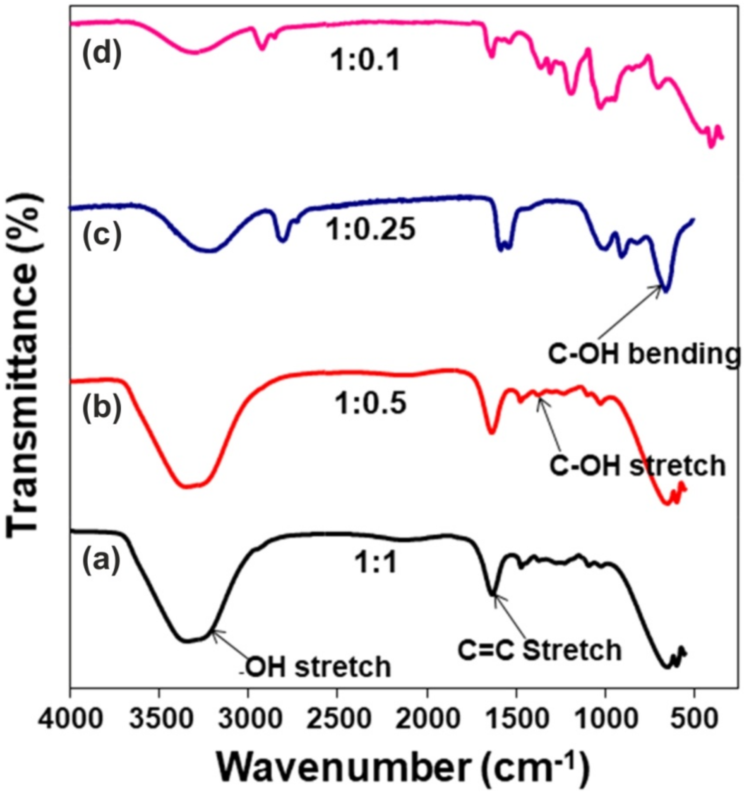

Figure 5.10 FTIR spectrum of PVA:RF with ratios (a) 1:1 (b) 1:0.5 (c) 1:0.25 (d) 1:0.1.

5.4.3 FESEM Analysis

5.4.3.1 FESEM Analysis of PVP:RF, PVP/PVA:RF and PVA:RF Gels

Field emission scanning electron microscope (FESEM) was used to investigate the morphological structures of synthesized PVP:RF, PVP/PVA:RF and PVA:RF polymeric blend gels. It has been observed that PVP:RF **(Figure 5.11a)** shows a rough surface of the gel system. PVP/PVA:RF (**Figure 5.11b**) confirms that the granular appearance of PVA:RF and rough appearance of PVP:RF disappeared and changed to a 3-D gel network system. This observation suggests the formation of a new type of gel network. PVA:RF **(Figure 5.11c)** gel system is having granular morphology. This polymeric gel system has a structure with several smaller agglomerates joining. In all **Figures**, the gel systems containing different polymers are having a special network structure because of crosslinker, which helps in connecting the polymeric chains more strongly.

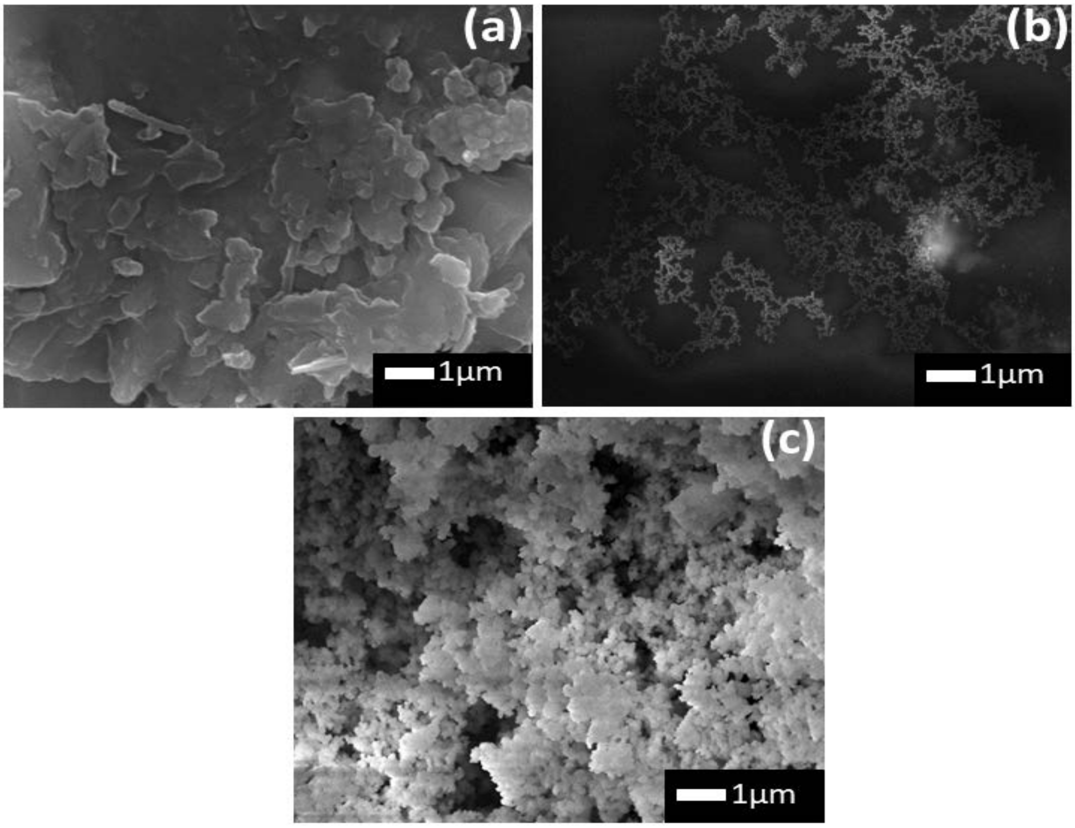

Figure 5.11 FESEM micrographs of (a) PVP:RF (b) PVP/PVA:RF and (c) PVA:RF (at 10,000×).

5.4.3.2 FESEM Analysis of PVP:RF, PVP/PVA:RF and PVA:RF Gels Before and After Sandpack Flooding

In **Figures 5.12 (a-c)** gels show that the original gel samples (before in-situ study) have an obvious strong 3-dimensional structure. For original gel samples, it is demonstrated that the preliminary net structure of gels is formed. It was confirmed by SEM images **Figures 5.12 (a-c).** In contrast, the effluents of gel samples after flowing through porous media did not show an obvious network structure as observed in original samples. It is shown in **Figures 5.12 (d-f).**

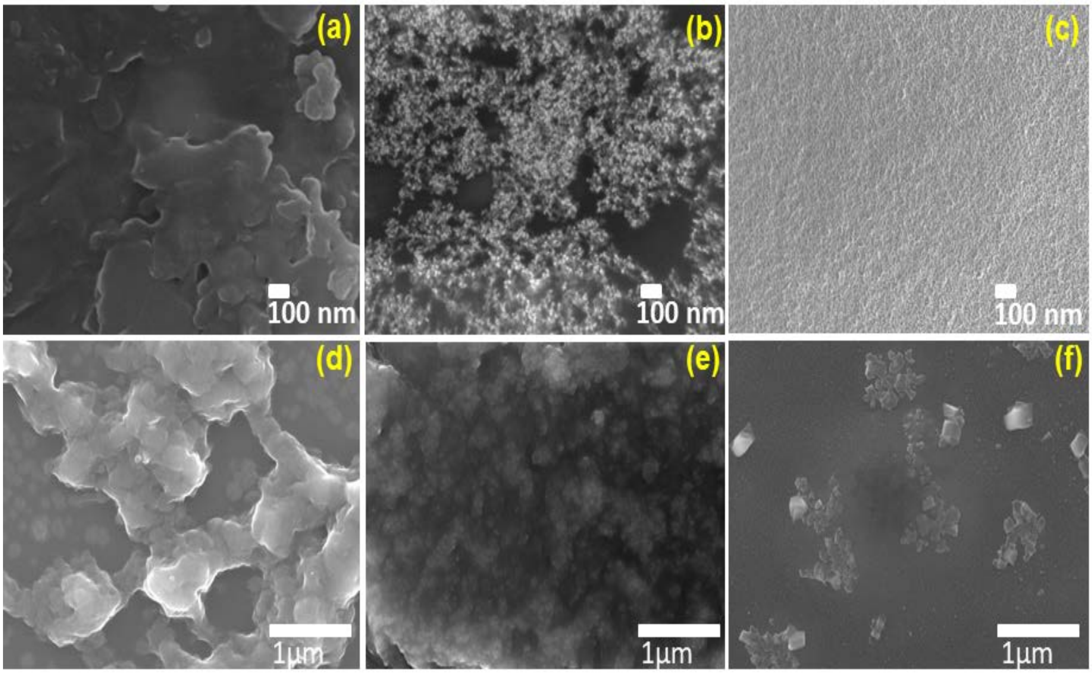

Figure 5.12 FESEM images of the fresh and effluent (flowing through porous media) gel samples (a, d) PVP:RF (b, e) PVP/PVA:RF (c, f) PVA:RF.

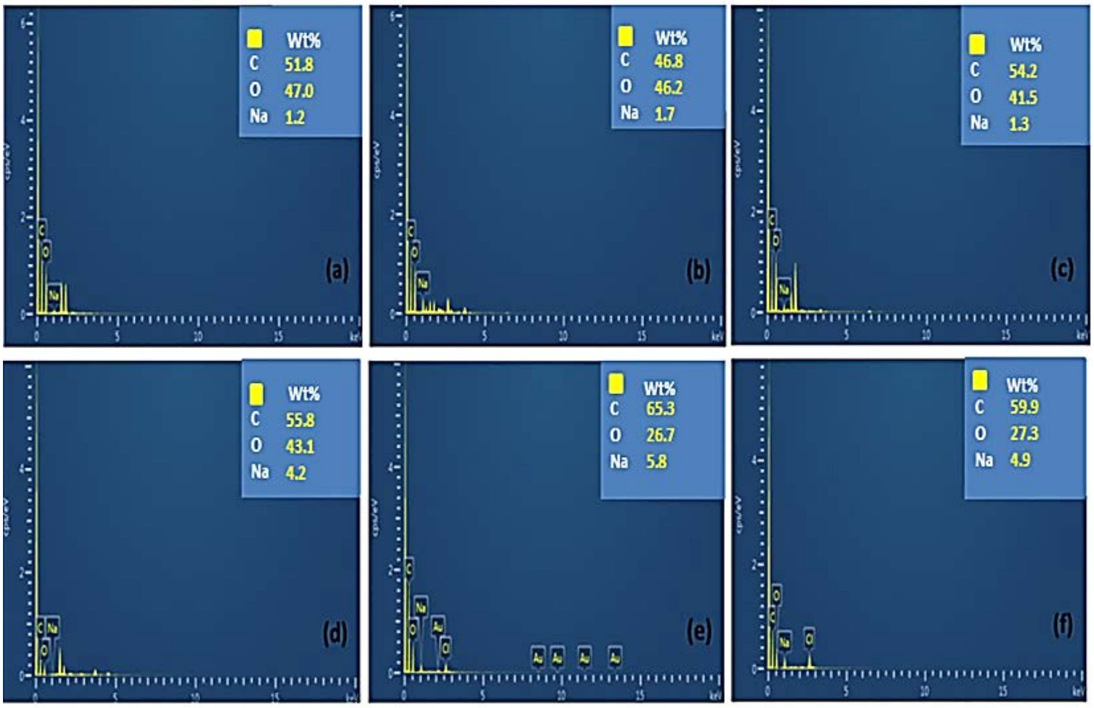

Figure 5.13 EDX spectra of PVP:RF, PVP/PVA:RF and PVA:RF gels respectively, before and after gel flooding (a-c) Fresh gel samples (d-f) Effluent gel samples.

The presence of high amount of salt can be seen in SEM images of effluent gel samples in comparison to original gel samples. A comparison of all three gel samples before and after in-situ study confirms that the gel strength of gel samples apparently reduced after flowing through porous media. The addition of brine in the effluent of gel samples is the reason for the reduction in viscosity. The addition of brine in the effluent of gel samples may be the reason for the reduction viscosity. Energy dispersive x-ray (EDX) data is given in **Figures 5.13 (a-f).**

5.4.3.3 FESEM Analysis of PVP:RF and PVP-ZnO:RF Gels

The structure of the synthesized nanoparticles was analyzed using SEM. The image in **Figure 5.14a** shows individual ZnONPs as well as aggregates and exhibits that the synthesized ZnONPs are spherical in shape. This result is in accordance with the one reported (Hiremath et al., 2017) where the ZnONPs have been synthesized using *Calotropis* leaf extract. **Figures 5.15 (a-c)** exhibits the image of PVP:RF conventional and PVP-ZnO:RF nanocomposite gels. These gel systems were dried, and their surface morphologies were examined using FESEM. It can be observed from the surface morphology of PVP:RF conventional gel (**Figure 5.15a**) that it has a smooth surface. FESEM images of PVP-ZnO:RF nanocomposite gels (**Figures 5.15b and 5.15c**) reveals significant alterations in surface morphology due to the presence of ZnO.

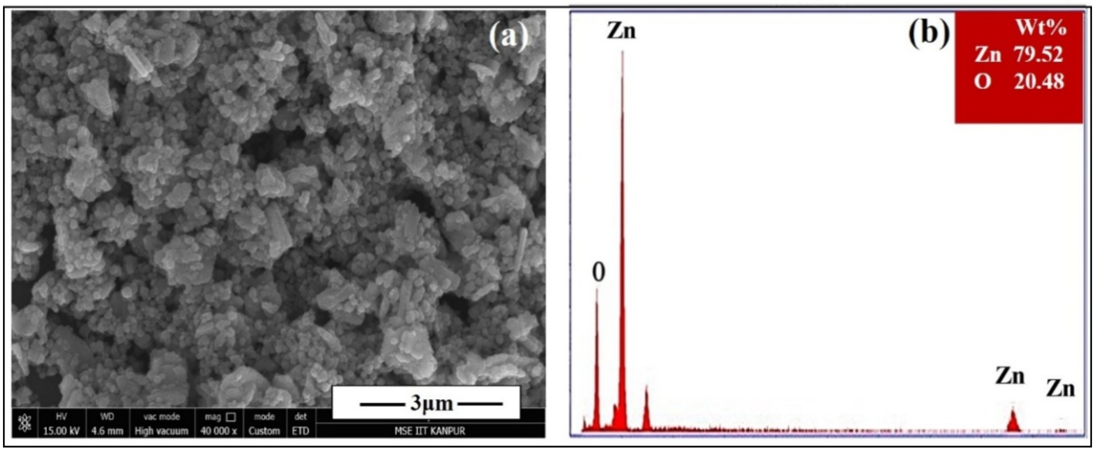

Figure 5.14 SEM image of ZnO nanoparticles at x 40,000and EDX data.

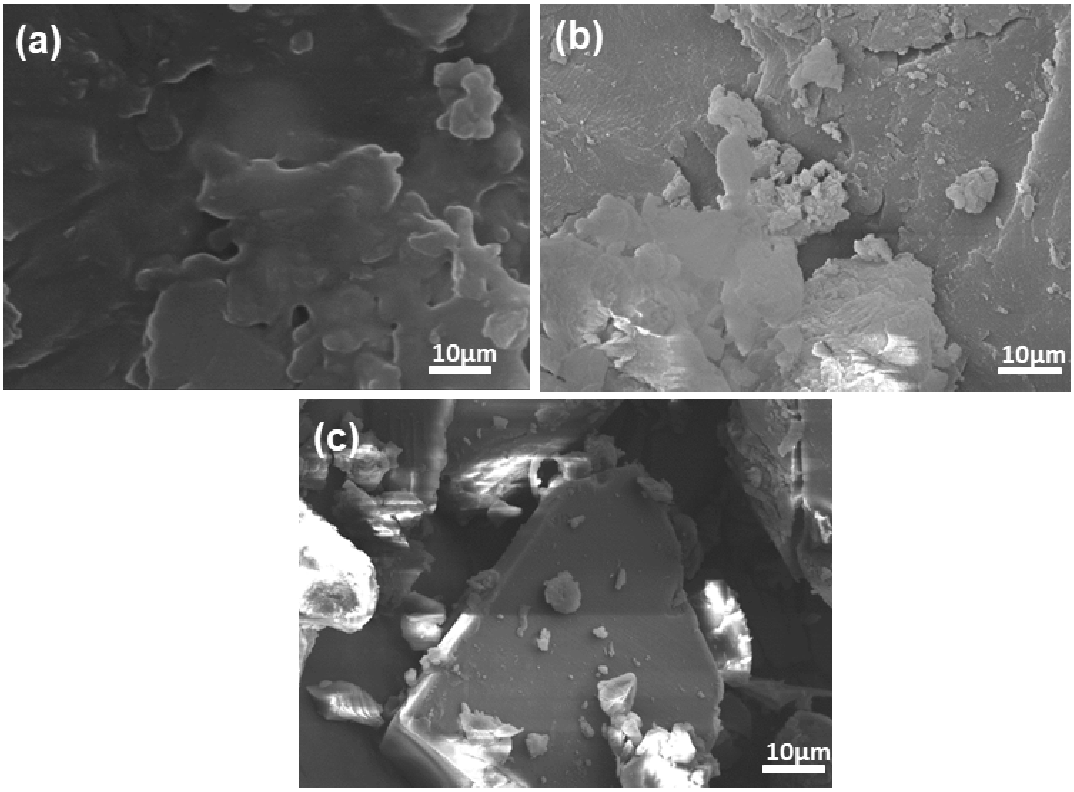

Figure 5.15 SEM micrographs of investigated gel systems at x 10,000 (a) PVP:RF (b) PVP-ZnO:RF (2000 ppm) (c) PVP-ZnO:RF (5000 ppm).

5.4.3.4 FESEM Analysis of PVA:RF Gel Systems

The microscopic images of different concentrations of the crosslinker with the polymer of the prepared gel system at 100 nm scale were achieved using FESEM to examine the morphological features as shown in **Figure 5.16.** These were studied for the mechanism of gel formation with different crosslinkers ratio. As shown in **Figures 5.16A and 5.16B**, the polymeric gel systems are having a special network structure because of the high concentration of crosslinker. The high concentration of crosslinker helps in connecting the polymer chains more strongly. More homogeneous morphology was obtained with 1:0.25 and 1:0.1 ratio of PVA:RF as shown in **Figures 5.16C and 5.16D**, for which the RF can be presumed to be homogeneously dispersed in the PVA matrix and shows fewer crosslinks. However, at a higher composition, the surfaces become rougher suggesting that the RF is in oversupply leading to phase segregation.

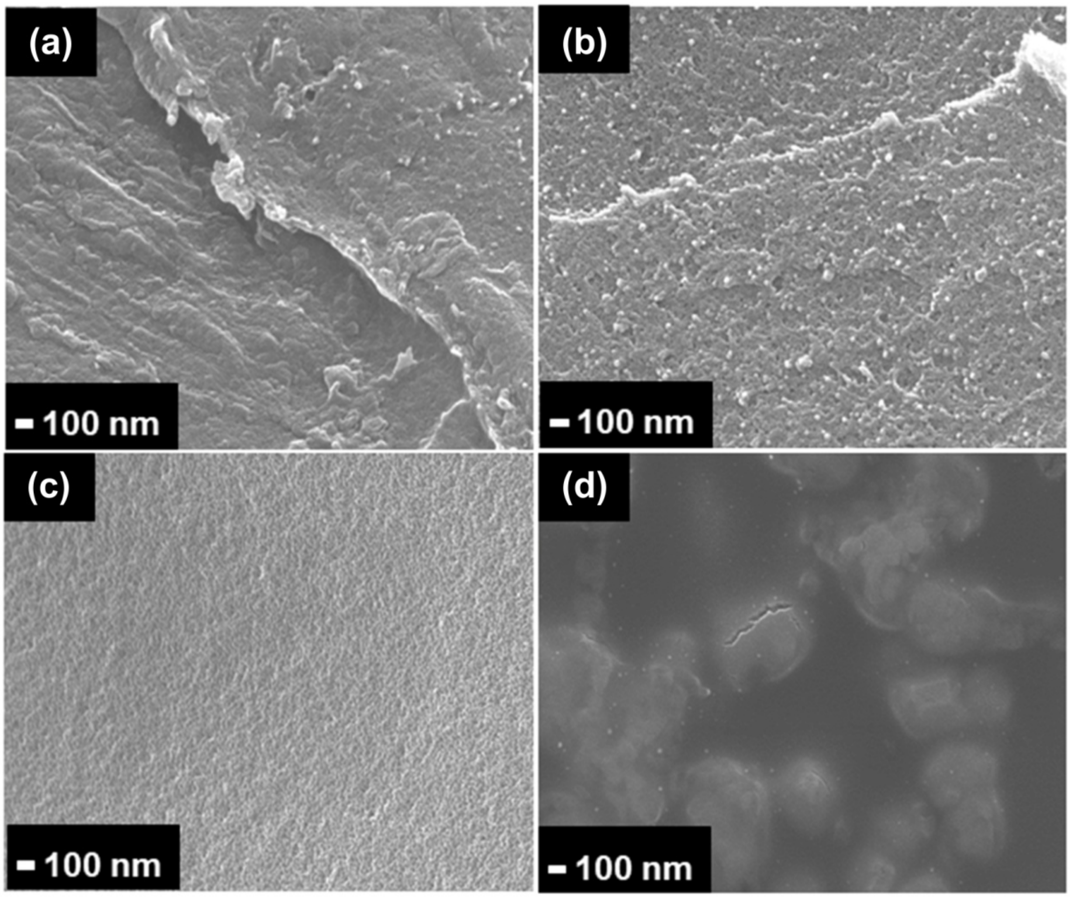

Figure 5.16 FESEM images for different crosslinker concentrations of PVA:RF gel at 30,000 magnifications and 100 nm scale (a) 1:1 (b) 1:0.5 (c) 1:0.25 (d) 1:0.1.

5.5 Conclusions

- ZnO nanoparticles were successfully synthesized using *Moringa oleifera* leaf extract and its identity was characterized using UV-Vis and XRD techniques.
- Intermolecular and intramolecular hydrogen bonding effect was checked using FTIR. Polyvinyl alcohol, polyvinylpyrrolidone are resorcinol-formaldehyde are hydrogen-bonded molecules. The result of the IR data shows intermolecular hydrogen bonding between polymer and crosslinker. Apart from it, nanoparticle interaction with gel was also observed.

- The formation of the gel network was confirmed by FESEM. The FESEM images clearly show the smooth and rough surfaces of the gels.
- A proper network formation was seen in PVP/PVA:RF blend. ZnO nanoparticle interaction was also seen in PVP:RF nanocomposite gels. From the FESEM images of gels, it was confirmed that gel strength increases due to ZnO.
- In PVA:RF gels, on increasing crosslinker concentration, a compact gel surface formation took place.

CHAPTER 6

THERMAL AND RHEOLOGICAL INVESTIGATIONS

CHAPTER 6

THERMAL AND RHEOLOGICAL INVESTIGATIONS

6.1 Introduction

Rheology basically deals with the deformation and the flow behavior of materials. On applying different stress conditions, solid and liquid samples change their nature. Newtonian and non-Newtonian fluids are investigated by rheology (Lapasin, 2015). Newtonian fluids are those which obey Newton’s law of flow. Samples, which fail to follow Newtonian’s law, are referred to as non-Newtonian fluids. Rheology defines the correlation between stress and deformation of samples. Polymeric gels are prepared by hydrogen bonding of polymer and crosslinker. These gels range from free flowing to ringing rigid gel, therefore, they exhibit a wide range of rheological properties. Polymeric gels are widely used in the upstream oil industry to control excessive water production. These gels are viscoelastic fluids (Cuomo et al., 2019). Viscoelastic fluids have the properties between elastic solids and viscous liquids. In polymeric gels, viscous nature leads over lesser time and elastic nature leads to long time duration. The gel strength of the gel is measured by rheology experiments (Zhao et al., 2017). The concentration of polymer and crosslinker changes gel strength of gels. Change in the strength of gels on the basis of change of components is measured by rheological tests. High gel strength is related to the higher stability of gels. Rheology is a qualitative and quantitative study of gels that describes relationships between shear stresses and strains or some other derivatives (Sgambato et al., 2016).

The response of polymers to heat or thermal properties is being investigated by using differential scanning calorimetry and thermogravimetric analysis. DSC is used to study the thermal transitions of polymers (Rodriguez et al., 1996). Qualitative and quantitative information about chemical and physical changes in gel samples is measured by DSC technique. Glass transition temperature is missing in our study because of the high crosslinking of gels. The melting point of the gel samples is investigated in our study. In TGA, physical properties of the gel sample are measured as a function of temperature or temperature (Tang et al., 2017). It can also be described as weight loss of a sample in an environment heated or cooled at a controlled rate and is recorded as a function of time and temperature.

In this chapter, the thermal and rheological study of conventional and nanocomposite gels have been described. Thermal and rheological properties of developed gels change when polymer or crosslinker or nanoparticle concentration varies.

6.2 Methods

6.2.1 Thermogravimetric Analysis

The thermogravimetric analysis technique was used to detect the response of the nanocomposite gel system and the conventional gel system against rising temperatures. The basic principle of the technique is to raise the temperature of the sample below its melting point. A reduction in the weight of the sample is observed due to the evaporation of water present in gel networks. Thermogravimetric analysis (TGA, Linseis PT 1000) of the synthesized gels was carried out in the nitrogen atmosphere by maintaining the heating rate of 3°C min^{-1} from 40 to 120ºC.

6.2.2 DSC Analysis

The differential scanning calorimetry profiles of the samples were recorded on a DSC 4000 from Perkin Elmer under N_2 atmosphere (20mL/min). Pre-weighed (~10mg) polymeric blend samples were taken in an aluminum pan for the measurement. The samples were heated from -20 to 200°C at a rate of 3°C/min. with sample mass comprised of 10-20 mg in the crucible. An empty sample pan was used as a reference.

6.2.3 Viscosity and Rheological Properties of the Bulk Gels

To analyze the strength of the prepared gel systems with different crosslinker concentrations, viscosity (η) and viscoelasticity (storage modulus G' and loss modulus G'') were measured by the cone-plate sensing system using a compact rheometer (MCR-52, Anton Paar®, Physica, Austria). These measurements are essential and deal with the deformation and flow of matter as a function of shear deformation. All the rheological properties were acquired in a controlled rate mode (CR). The shear viscosity, elastic and viscous modulus (G' and G'') were used to evaluate the structural recovery property of the gel after shear action. The elastic and loss modulus dependent on frequency and amplitude shows viscous and elastic part of the sample and it is measured when a stress is applied to the sample. The shear viscosity was measured as a function of temperature and shear rate. Shear rate was fixed to be 1 Hz during the temperature effect on shear viscosity. During the amplitude sweep, the frequency was fixed at 1 Hz and frequency sweep was carried out from 1 Hz to 100 Hz at fixed amplitude so as to remain in the linear viscoelastic regime. The temperature dependence of viscosity was studied in the temperature range of 30-80°C.

6.3 Results and Discussion

6.3.1 Effect of ZnO Nanoparticles on TGA Analysis

The effect of ZnO particles inside the gel network was confirmed by the thermal analysis. **Figure 6.1** shows the TGA curves of PVP:RF and PVP-ZnO:RF gel systems. TGA was performed to determine the percentage weight loss of prepared gel systems. The TGA curves show a feature between 50-90ºC, which indicates a large weight loss of all three samples. This mass loss was due to the characteristic thermal behavior of hydrogels. The remaining mass of all samples as measured by TGA was 2.58% (PVP:RF), 5.73% (PVP-ZnO:RF, 2000 ppm) and 9.64% (PVP-ZnO:RF, 5000 ppm) at 110ºC. The result of different gel systems indicates the effect of ZnO on the strength of the gel. From the observations of the current study, it can be concluded that nanocomposite gel systems show higher thermal stability in comparison to the conventional gel system (Heo et al., 2014).

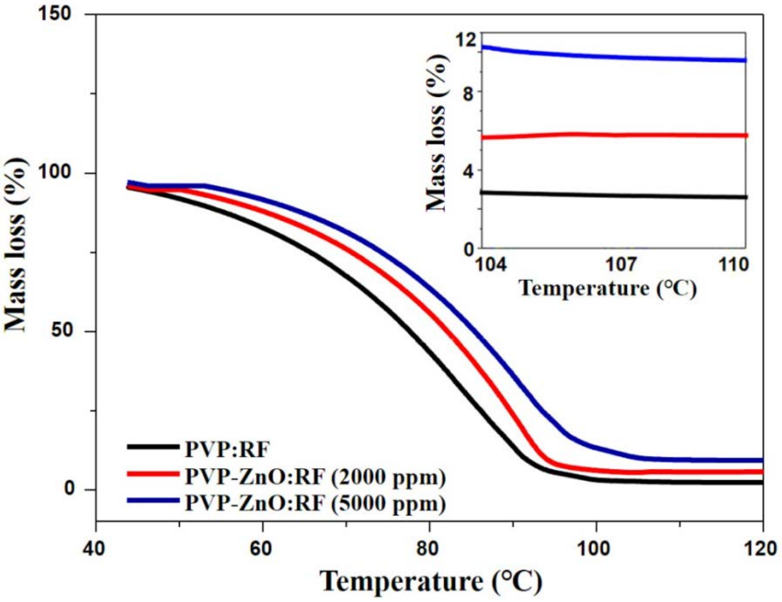

Figure 6.1 Thermogravimetric analysis of different behavior for PVP:RF, PVP-ZnO:RF (2000 ppm) and PVP-ZnO:RF with (5000 ppm).

6.3.2 Differential Scanning Calorimetry (DSC) Analysis

An important factor in the development of the new materials based on polymeric blend is miscibility between the polymers in the mixture because the degree of miscibility is directly related to the final properties of polymeric blend gel. There are many studies related to the miscibility of PVA and PVP (Huang et al., 2017; Nguyen et al., 1994). In the present study, the miscibility of PVP/PVA:RF blend was confirmed by DSC. **Figures 6.3 (a-c)** shows the DSC thermograms for the thermal behavior of PVP:RF, PVP/PVA:RF and PVA:RF polymeric gel systems. Polymer and the crosslinker ratio were the same in all samples i.e., 1:0.25. The scanning temperature ranges were from -20 to 200ºC and the heating rate was 3ºC/min. Gel samples were prepared at 90ºC. The bond strength of the interaction between polymer and crosslinker can be determined by how much energy is required to break the bonds between polymer and crosslinker. This energy is referred to as degradation enthalpy. The stronger the interaction, the more endothermic energy is required to break down the bonds in gel systems. Conquering a higher degree of enthalpy would suggest the formation of a strong bond between polymer and crosslinker thus producing a gel with high gel strength. In addition, the temperature at which the crosslinked chains of the gel systems start to breakdown is known as the degradation temperature. At this temperature, the mobility of PVA and PVP chains increases. There are many possible direct and indirect interactions, which are responsible for strong and weak gel network. These both type interactions take place due to the hydrophilic nature of the polymer and crosslinker, which could form hydrogen bonds with water molecules. Indirect interactions take place as free or bound water. The free water is referred to as the absorbed water that is, water molecules attached to other water molecules via hydrogen bond. Meanwhile, the bound water refers to water that is chemically bound to the surface as depicted in **Figure 6.2** (Liu et al., 2017).

In other words, the presence of bound water decreases the availability of direct interactions. It leads to a weak gel network. Therefore, in the presence of higher bound water, less endothermic energy is required to break the bond between polymer and crosslinker. The bound water and free water can be calculated from the endothermic peak from 0 to 7ºC temperature through the following equation found in the literature (Asadizadeh et al., 2019; Liu et al., 2017; Michael et al., 2018):

$$W_b = \left({}^{\Delta H}/_{\Delta H^{o}}\right) \qquad \text{..... (viii)}$$

$$W_f = 1 - W_b \qquad \text{..... (ix)}$$

Where, W_b is the fraction of bound water, W_f, the fraction of free water, ΔH, the enthalpy required for heating the free water in the gel and ΔH^o is the 333.5 J/g standard degradation enthalpy for free water.

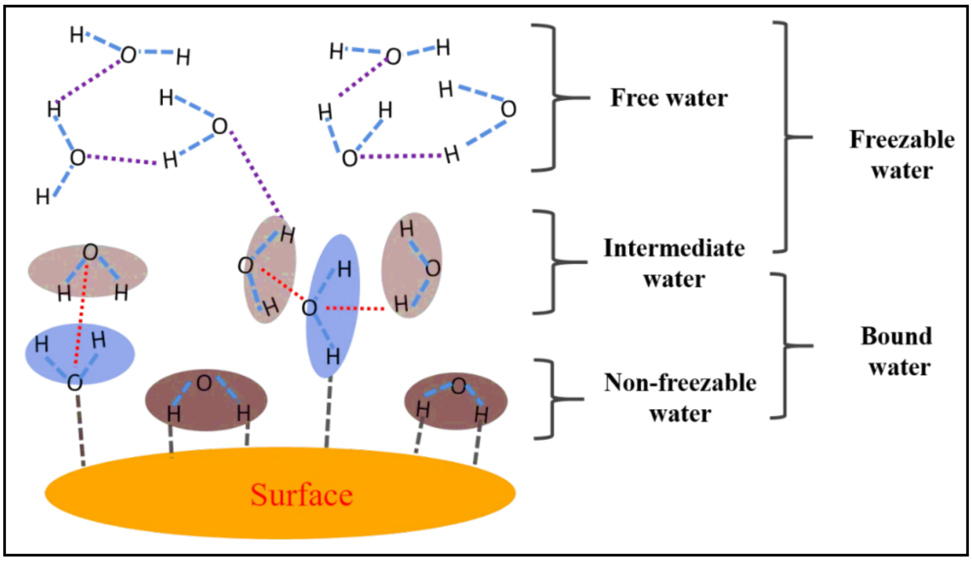

Figure 6.2 Water bonding types in gel and representation of free and bound water (Michael et al., 2018).

Two peaks were detected in the DSC curves of gel samples. The first peak is representing the presence of free water in the gel systems and the second peak represents the degradation temperature (T_{deg}) of the gel systems. It was observed that PVP:RF gel system had higher free water, however, PVA:RF gel system had less free water.

From **Figures 6.3 (a-c)** samples, it can be seen that when PVP concentration decreases, degradation temperature also decreases. From DSC results, it can also be observed that PVP:RF and PVP/PVA:RF samples show degradation at a higher temperature than PVA:RF. This could be due to the restriction of chain mobility of PVP and PVP/PVA (polymer and blend) due to strong hydrogen bonding (Abdelrazek et al., 2010; Nishio et al., 1990; Schindler et al., 2017; Yi et al., 2005).

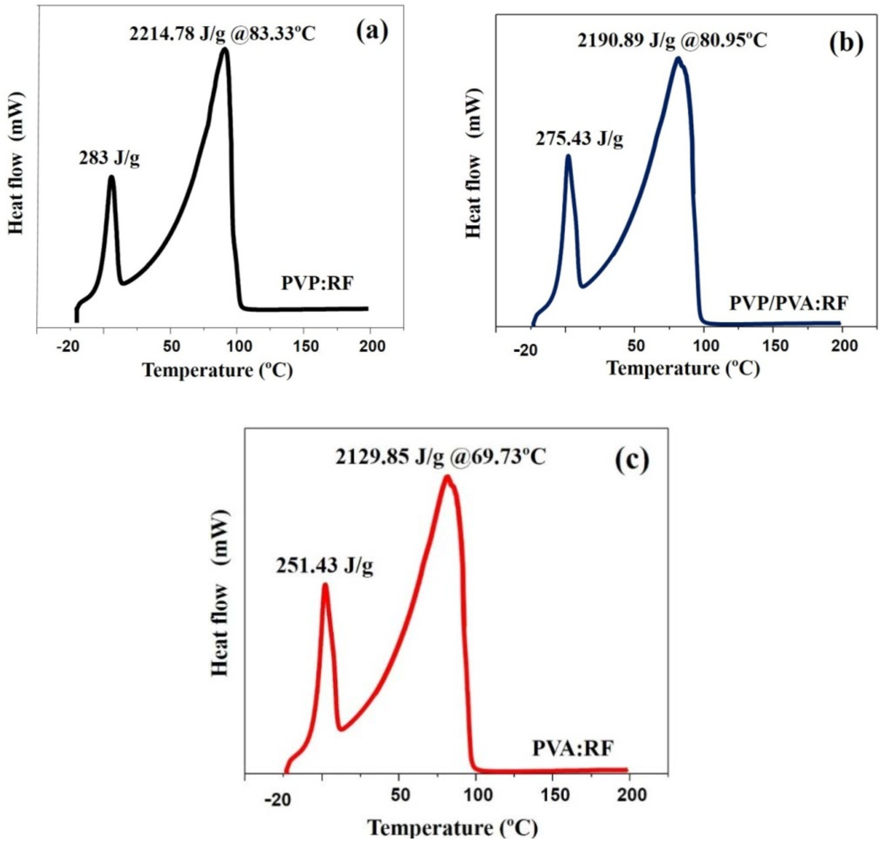

Figure 6.3 DSC thermographs for all gel systems including free water evaporation and degradation peak (a) PVP:RF (b) PVP/PVA:RF (c) PVA:RF.

6.4 Rheological and Viscoelastic Measurements of Gels

6.4.1 Rheological and Viscoelastic Measurements of PVP:RF, PVP/PVA:RF and PVA:RF Gels

6.4.1.1 Shear Rate Dependent Viscosity Test

Figure 6.4 demonstrates the viscosity vs shear rate plot for all samples. The flow curves for PVP/PVA:RF blend was similar to that of the PVA:RF and PVP:RF gels. The results prove that the shear viscosity of all the blends decreases with increasing shear rate, which is typical of viscoelastic non-Newtonian or shear-thinning viscoelastic. Polymeric blend showed shear viscosity, which is lower than PVP:RF and higher than PVA:RF gel systems. However, PVP:RF showed higher viscosity than PVA:RF and PVP/PVA:RF gel (Chand et al., 2014).

The lower viscosity of the PVA:RF gel system could be attributed to a decrease in the semi-crystalline property of PVA due to the presence of salt. The decrease in the shear viscosity could be attributed to the alignment of chain segments of all the samples in the direction of applied stress. **Figure 6.4** again shows that the shear viscosity is constantly decreasing and it can be predicted that all the blends showed a Newtonian molten flow. It indicates the same behavior of polymer gels and polymeric blend gel. The dependence of shear viscosity on the shear rate at all shear rate regime is more pronounced as the amount of gel component varied. The increase in viscosity was probably due to increased interaction between hydroxyl groups or hydrogen bonding.

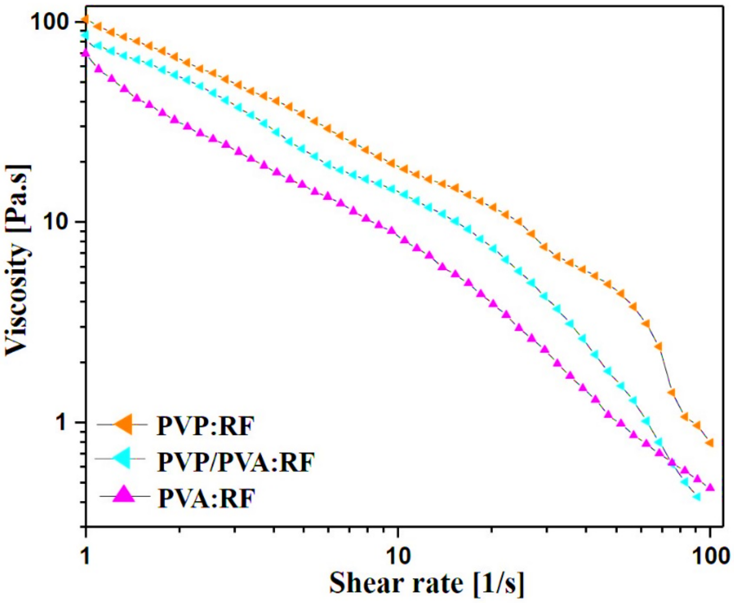

Figure 6.4 Shear thinning behavior graph of PVP:RF, PVP/PVA:RF and PVA:RF gels.

6.4.1.2 Frequency Sweep Test

The frequency (ω) or rate of deformation dependence on elastic (G’) and viscous (G”) moduli of the gel samples were further tested by sweeping the frequency (1 Hz to 100 Hz) at a constant strain. To determine the mixing of two polymers on the stability of gels. As given in **Figure 6.5**, it can be seen that within the frequency range tested, the storage modulus (G’) increased with increasing frequency. The curves of G’ versus ω followed almost a linear mixing rule (Arsad et al., 2013). It was found that the value of G’ of the polymeric blend was in between PVP:RF gel and PVA:RF polymeric gel. That indicates the formation of a new structure in this blend. It was believed that the interaction has occurred among PVA, PVP, and RF. It can be attributed that new copolymer formations took place at the interface of the blend. The interaction can stabilize the interface by reducing the coalescence and interfacial adhesion and viscosity.

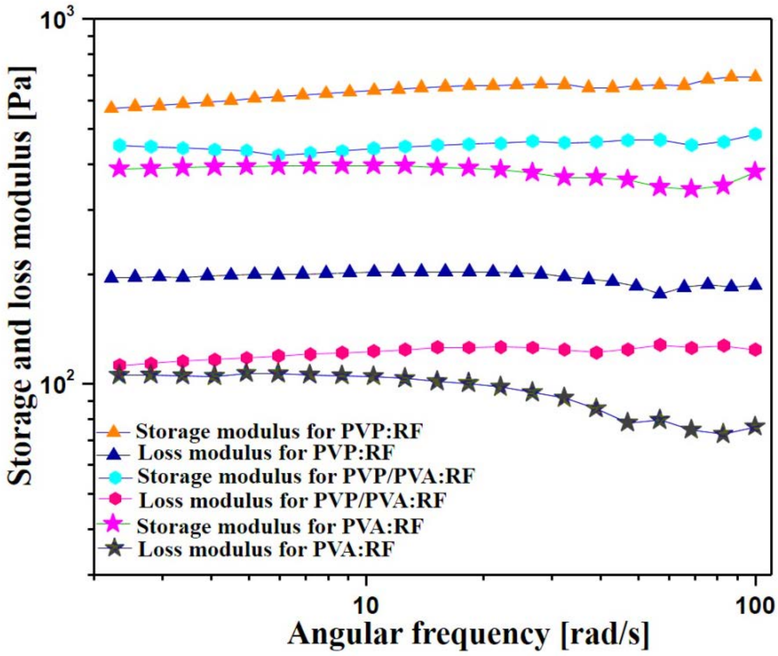

Figure 6.5 Frequency dependent storage and loss modulus graph of PVP:RF, PVP/PVA:RF and PVA:RF gels.

On the other hand, it should be emphasized that PVP:RF and PVA:RF gels have high viscosity and low viscosity respectively. However, the viscosity of PVP/PVA:RF blend gel is in between these two gel systems having desired viscosity. This phenomenon of blend could be attributed to set the desired relaxation time due to the decrease in semi-crystalline property of PVA due to the blending of PVP in gels.

The response of loss modulus G” against frequencies of different gel samples is represented in **Figure 6.5**. As far as G” is concerned, PVP:RF produced a higher loss modulus and PVA:RF produced a lower loss modulus. That indicates higher energy dissipation compared to PVA:RF with PVP:RF. This indicates that the viscous components of the blends could be changing the concentrations of PVA, PVP, and RF.

6.4.1.3 Complex Viscosity Dependent Frequency Graph

The complex viscosity dependence on the frequency of gels and polymeric gel blend is shown in **Figure 6.6**. From the Figure, it is clear that PVP:RF shows higher complex viscosity than PVP/PVA:RF and PVA:RF gel systems. Therefore, the data indicated that the viscosities of different gel systems can be changed by changing polymers i.e., PVA, PVP and blend of these two. The blending of polymer gel resulted in significant changes in their rheological properties.

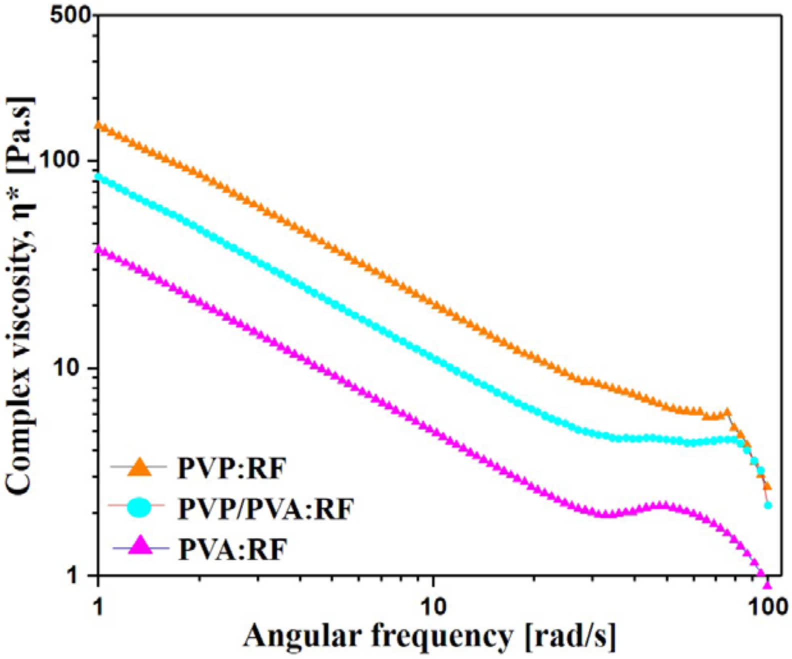

Figure 6.6 Complex viscosity versus frequency graph of PVP:RF, PVP/PVA:RF and PVA:RF gels.

In general, the polymeric blend gel and pure polymeric gels presented a typical behavior, exhibiting a shear-thinning regime at all frequencies studied. The material exhibits solid-like nature if G' is more than G”, or liquid-like behaviour, if G” is more than G’. Therefore, from results, it could be ascribed that gel systems showed a solid-like characteristic and can be categorized as viscoelastic materials.

6.4.2 Effect of ZnO Nanoparticles on Rheological Properties of the Gels

6.4.2.1 Shear Rate vs Viscosity Analysis

The viscosity vs shear rate graphs for all three samples are depicted in **Figure 6.7** given below. The deformation behavior of prepared gels can be described by plotting shear rate dependent viscosity graph. On increasing shear rate viscosity decreases. These trends indicate the shear thinning nature of gels (Chand et al., 2014).

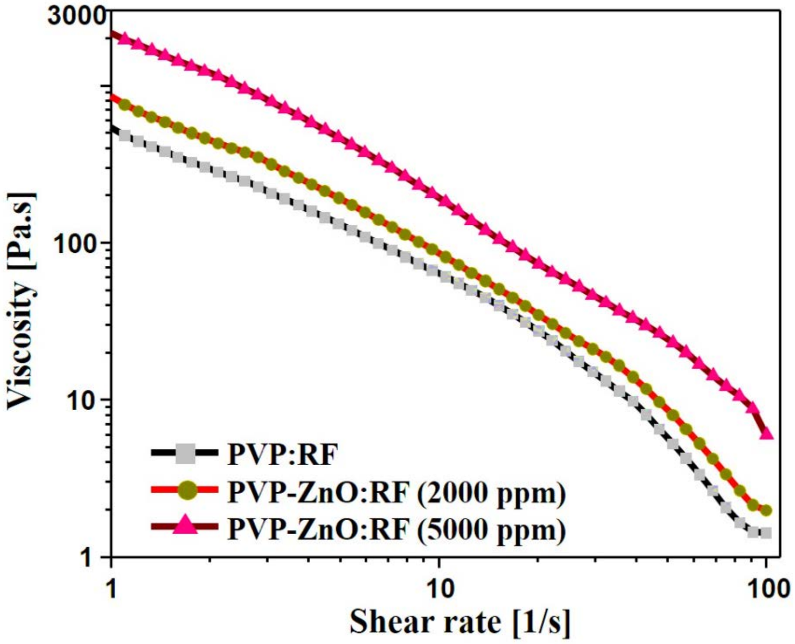

Figure 6.7 Shear thinning behavior of PVP:RF, PVP-ZnO:RF (2000 ppm)and PVP-ZnO:RF (5000 ppm).

6.4.2.2 Frequency Sweep Analysis

To determine the rheological properties of conventional and nanocomposite gel systems, the frequency sweep test was conducted. The frequency range was 1Hz to 100Hz at a constant strain of 1.0% at room temperature. It was observed from the result that the elastic modulus (G’) values are higher than loss modulus (G’’) as shown in **Figure 6.8**. It indicates that the value of elastic modulus is dominating over the value of viscous modulus. These results indicate solid or rubber-like characteristic of gel systems and there is also no crossover or gel point although we go to very low frequency. At this point, we have reached a gel, solid-like behavior. The values of modulus show that interaction between particles of the formed network is very high and physical forces act as a bond. Nanocomposite gel showed higher elastic and loss modulus than conventional gel (Arsad et al., 2013).

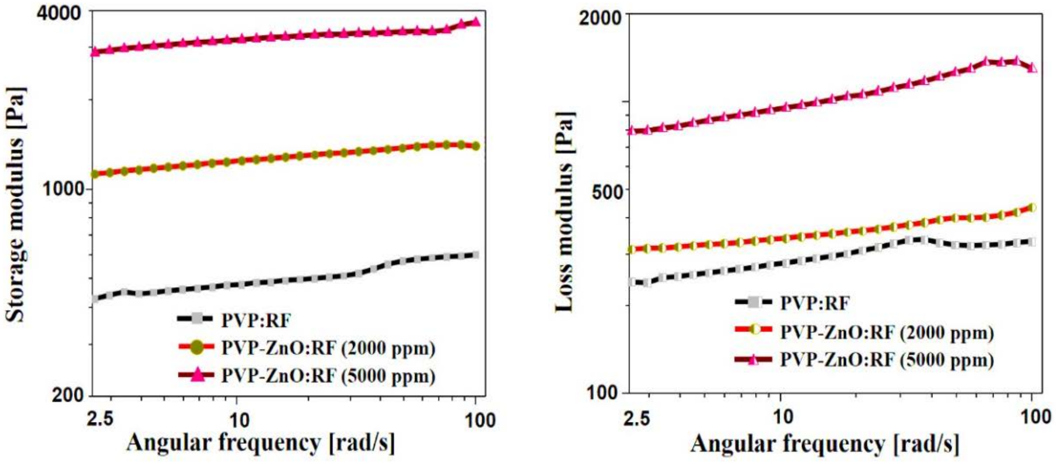

Figure 6.8 Frequency dependent storage and loss modulus graph for different behavior for PVP:RF, PVP-ZnO:RF (2000 ppm) and PVP-ZnO:RF with (5000 ppm).

6.4.3 Rheological and Viscoelastic Measurements of PVA:RF Gels

To carry out rheological experiments, 4 different gel systems (1:1, 1:0.5, 1:0.25 and 1:0.1) aged for 24, 48, 144 and 168 hours respectively at 90℃ temperature were selected. Viscous properties dependent on temperature (this measurement was carried out at temperature range from 30-80°C) and shear rate and viscoelastic properties, storage and loss modulus **(**G’ and G’’**)** dependent on frequency and amplitude were determined at room temperature**.**

6.4.3.1 Strain Sweep Test

The gel strength i.e., up to what extent, the polymeric gel deformation takes place without tearing of the gel network and the determination of the linear viscoelastic region of the gel system are the two most important points during the placement of the gel into the reservoir. This strain sweep test was carried out at a constant frequency of 1 H_z for all four samples of PVA:RF as shown in **Figure 6.9.** The polymeric gel systems were prepared at room temperature and aged for different time intervals at a temperature of 90˚C. It was found that for PVA:RF 1:1 gel system, elastic modulus is higher and for 1:0.1 is lower as shown in **Figure 6.9** given below. It shows that for all ratio of PVA:RF, the value of elastic modulus and loss modulus is almost constant until up to 0.01% values of strain. Consequently, it shows a similar response to Hookian behavior and that area is called the linear viscoelastic region. Also, we can see, that the values of G' are much higher than G" values, which show that the elastic nature is dominant over viscous nature.

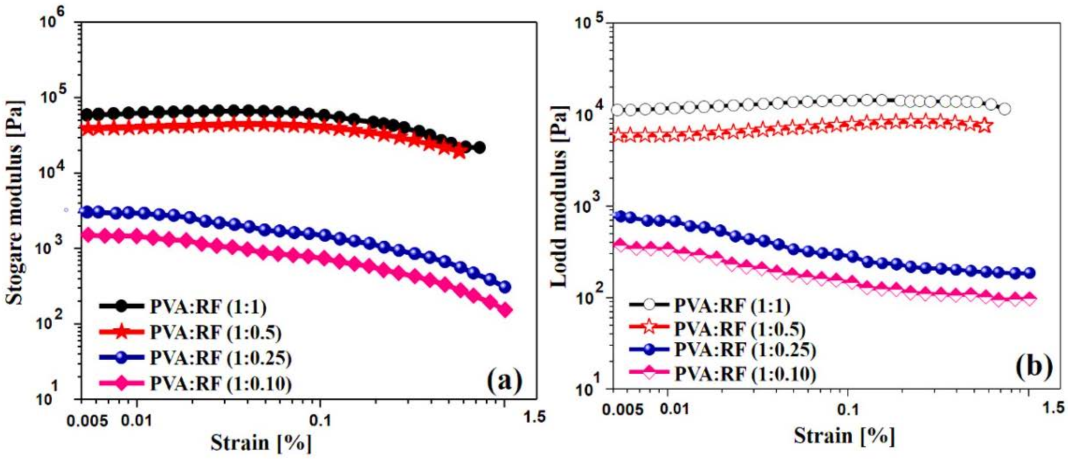

Figure 6.9 Amplitude dependent (a) storage modulus (b) loss modulus graph for crosslinker concentrations of PVA:RF gel at room temperature.

From 0.01% to 1.0%, the values of the elastic modulus as well as viscous modulus decrease for all PVA:RF ratio, which shows the non-linear viscoelastic region of gel systems. **Figures 6.9a and 6.9b** shows that the strength of the gel system increases when the concentration of crosslinker increases (Chand et al., 2014).

6.4.3.2 Temperature Dependent Viscosity Test

Temperature dependent viscosity test was performed to examine the behavior of polymeric gel in the temperature range of 30-80°C and the graph leading to it is shown in **Figure 6.10.** The viscosity of all gel samples was found to be dependent on the temperature**.** As the temperature of these gels increases, viscosity decreases**.** Precise measurements of these gel samples are essential for using the gelant solution in coreflood studies**.** The time scale of the rheometer with temperature was around 15 minutes but that for the gelation kinetics is over 48 hours.

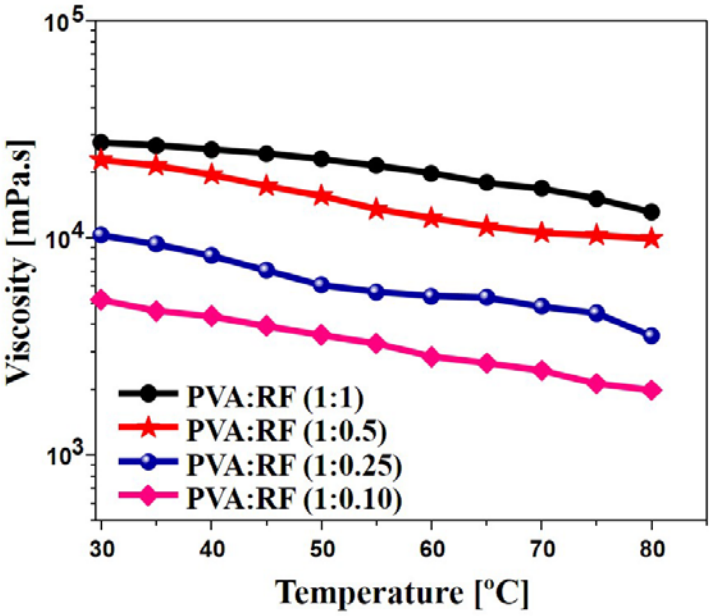

Figure 6.10 Temperature dependent viscosity graph for different crosslinker concentrations of PVA:RF gel from a temperature range 30-80°C.

6.4.3.3 Shear Rate Dependent Viscosity Test

Figure 6.11 shows the effect of different concentrations of crosslinker **(**RF**)** on PVA:RF gel at different shear rates**.** The results show that the shear viscosity of all the ratio of PVA:RF decreases with increasing shear rate, which is typical of viscoelastic non-Newtonian or shear thinning**.** The decrease in shear viscosity can be attributed to the alignment of chain segments of gels in the direction of applied stress**. Figures 6.11a and 6.11b** again show that the flow curves are different for 1:1, 1:0.5 and 1:0.25 and 1:0.1 combinations respectively**. Figure 6.11a** shows the variation in viscosity with shear rate **(**0**.**001 - 1 s^{-1}**)**. In 1:1and 1:0.5, PVA:RF gel system, shear viscosity linearly decreases and shear rate increases**.** That behavior of gel systems could be attributed to that this system shows non-Newtonian type characteristics at the low shear rate as well high shear rate or there is a drastic change in microstructure properties of gel from equilibrium even when the shear rate is low**.** In softer samples, the shear thinning effect is not as prevalent**. Figure 6.11b** shows the variation in viscosity with shear rate **(**1-100 s^{-1}**).** It indicates that, at a lower shear rate, the viscosity change is very low, and it can be predicted that these gels showed a Newtonian molten flow**.** Thus, there is not much change in non-Newtonian behavior at a lower shear rate compared to 1:1 and 1:0.5, PVA:RF gel system**.** The viscosity increased with increasing the concentration of RF**.** The increase in viscosity was probably due to increased hydrogen bonding interaction between PVA and RF (Chand et al., 2014).

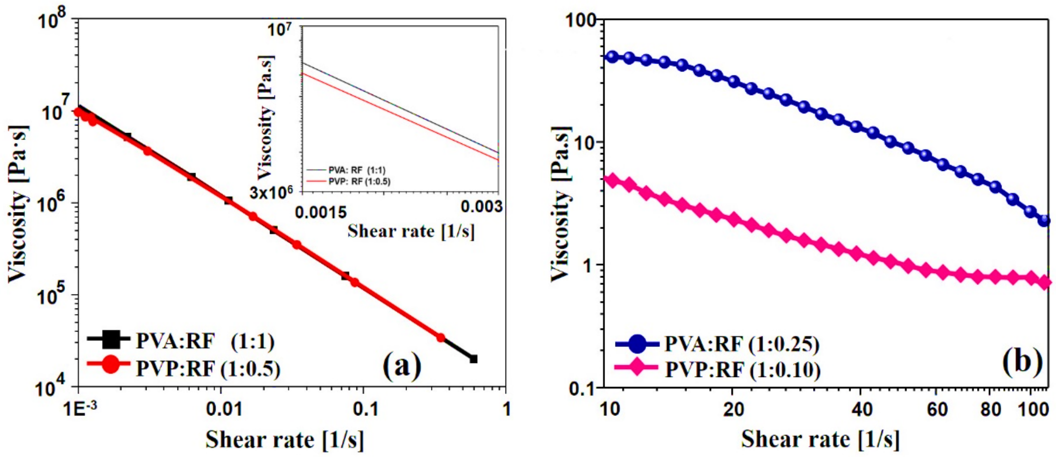

Figure 6.11 Shear thinning behavior of different crosslinker concentrations of PVA:RF gel (a) 1:1 and 1:0.5 (b) 1:0.25 and 1:0.1.

6.4.3.4 Frequency Sweep Test

Figure 6.12 displays the relationship between modulus and frequency (ω) for the PVA:RF gels containing different concentrations of RF. In **Figure 6.12a,** it can be seen that within the frequency range tested, the storage modulus increased with an increase in frequency. The curve of elastic modulus and frequency almost followed a linear mixing rule, which is at a static frequency; the storage modulus increased with increasing the amount of crosslinker. It was found that the value of G' of the PVA:RF gel was higher as compared to other gel systems with the whole frequency (rad/s) region, indicating different kinds of structure of these gel systems. As shown in **Figure 6.12a** for PVA:RF system, it could be attributed that the interaction has occurred between PVA with RF and formed copolymers at the interface of the gels. The interaction can stabilize the interface by reducing the coalescence and interfacial tension, resulting in enhancement of the interfacial adhesion and viscosity.

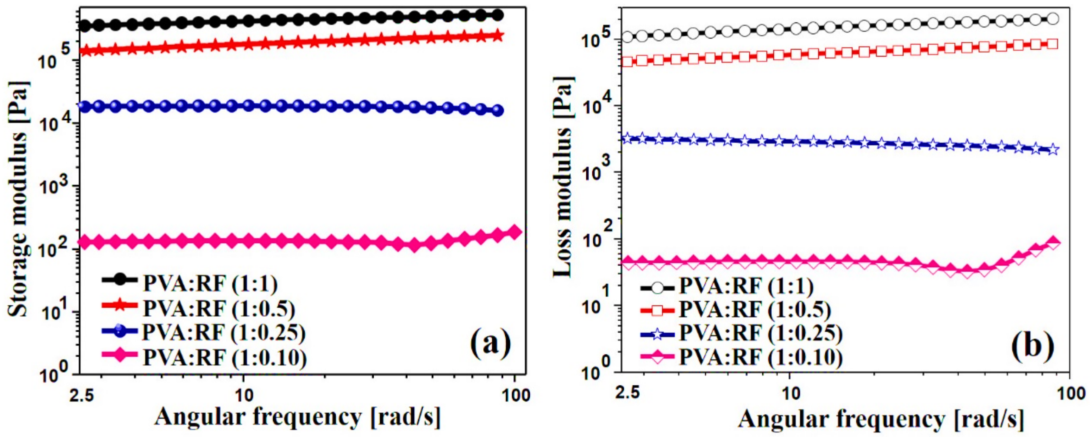

Figure 6.12 Frequency dependent (a) storage modulus (b) loss modulus graph for crosslinker concentrations of PVA:RF gel at room temperature.

Figure 6.12b shows the response of loss modulus (G”) vs frequency at different PVA:RF ratio. As far as G” is concerned, it can be seen that higher concentration of RF in the gel systems produce a higher viscous modulus, indicating higher energy dissipation compared to the gel systems with lower RF concentrations. These loss modulus responses of different PVA:RF concentrations appeared to deviate systematically from the behavior of all gel samples (Arsad et al., 2013).

6.5 Conclusions

- DSC data exhibited the thermal stability of all three gel systems and it may be confirmed that PVP:RF and PVP/PVA:RF gel systems showed good stability in comparison to PVA:RF.
- TGA analysis showed better thermal stability of nanocomposite gels (PVP-ZnO:RF) in comparison to conventional gel (PVP:RF).
- Viscosities of gel systems were determined as a function of shear rate and results demonstrated shear thinning behavior of gels. At a fixed frequency, the complex viscosity increased for PVP:RF system.

- The storage or elastic modulus(G’) and loss and viscous modulus (G”) were determined as a function of frequency and the result illustrated that elastic modulus is higher than the viscous modulus. It indicates the viscoelastic nature of gel systems.

CHAPTER 7

SANDPACK/CORE FLOODING STUDY

CHAPTER 7

SANDPACK/CORE FLOODING STUDY

7.1 Introduction

Excess water production in hydrocarbon reservoirs is one of the major issues faced by the upstream hydrocarbon industries. Due to excess water production problem, the reservoir becomes mature early than actual. The cost of separation, lifting, handling and disposal of this water is another big issue (Ma et al., 2007). Corrosion, emulsion, scale formation and environment unease are among the issues faced by the industries because of produced excess water. Subsequently, there is a need to reduce produced water. The objective of hydrocarbon industries is to get more oil from the existing oilfields under current circumstances (Hua et al., 2015). The new techniques have been to recuperate more oil and less water from the oilfields through some new strategies. Many EOR techniques, for example, water flooding, polymer flooding and so forth are in progress in numerous oilfields around the globe for the last several years. However, heterogeneity in the reservoir reduces the effectiveness of these EOR techniques. Ergun equation was used to calculate change in particle diameter in the core after gelation (Abirov et al., 2020).

The objective of this study is to evaluate the effectiveness of polymeric gel systems in sandpack and core in terms of permeability. Pre and post gelation permeability were determined. The RRF and PPR was calculated to determine the reduction in permeability.

7.2 Procedure

To test the effectiveness of the prepared gel systems for water shut-off purposes, a coreflood and sandpack study were conducted**.** In this study, the Berea core and sandpack was used. An experimental set up for this experiment is given in **Figure 7.1.** Ergun equation was used to change in the particle diameter.

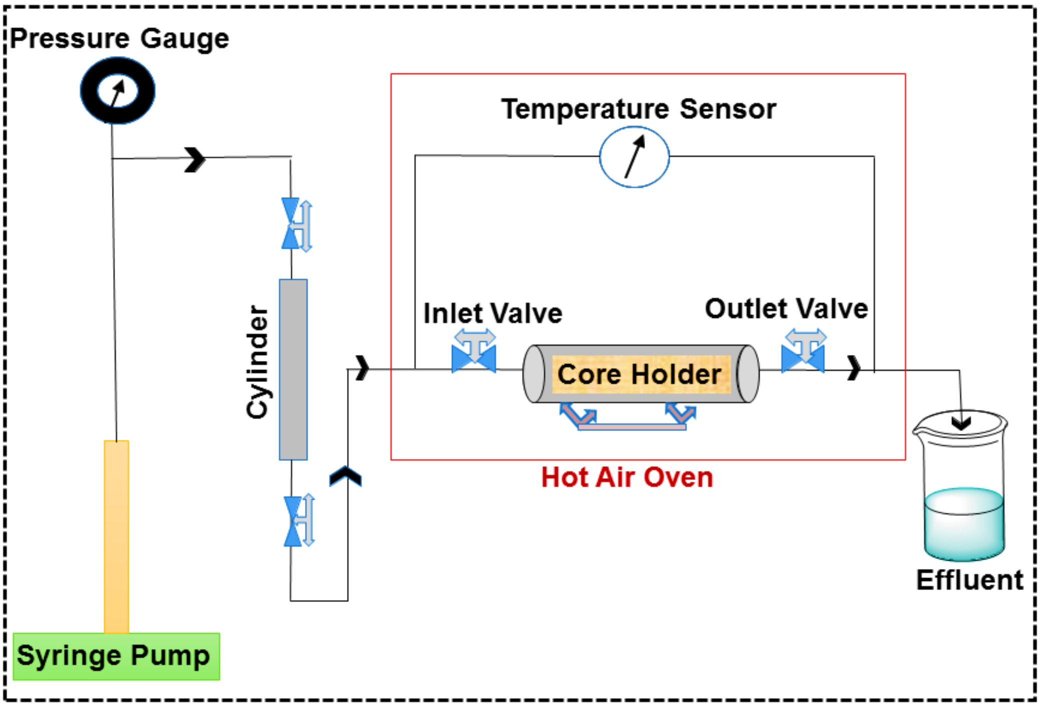

Figure 7.1 Schematic experimental setup for the sandpack or core flooding study.

7.2.1 Sandpack Flooding Study

For carrying out sandpack studies, sand used for the flooding experiments was collected from a commercial retail outlet, which was washed using toluene and dried in the oven for 48 hours at a temperature of 100ºC. The Sandpack was prepared manually in a cylindrical pipe (diameter: 3.81 cm and length 61.3 cm) made of stainless steel supplied by D-CAM Engineering, Ahmedabad, India through the bashing of dry sand together with 2.0% NaCl (brine). Sandpack holder consists of an electrical thermal jacket with a temperature controller to create the desired temperature during flooding experiments. The sandpack flooding setup consists of a horizontal sandpack holder, a syringe pump (100DX, Teledyne ISCO, USA), fluid accumulators and a flask to collect the effluent. A flow rate of 1mL/minute was used and kept constant in the process. Sandpack flooding experiments were started with the brine injection as preflush to ensure the water saturation (100%) in sandpacks. Absolute permeability to brine for each sandpack was determined using Darcy's law. Brine injection was followed by the injection of diesel oil in the sandpack until there was no more water produced as effluent. This is called the condition of irreducible water saturation (S_{wi}). The original oil in place (OOIP) was calculated using material balance calculations from the brine produced. This produced brine is considered as original oil in place. Again, sandpack was flooded with brine. All the solutions were injected in the sandpacks at a constant flow rate of 1mL/minute using a syringe pump and pressure drop across the pack was recorded. After injection of brine, 3-4 pore volumes of gelant was injected in the sandpack and the pack was shut-in for desired time to ensure the gel formation in the pack. After gel formation, brine, diesel oil and again brine were injected one by one to see the variation in permeability. Toluene was used as a pushing fluid in the study and temperature was kept 90ºC (Goswami et al., 2018; Chaturvedi et al., 2019). Darcy's law was used to calculate relative permeabilities of brine before and after gel treatments. After that, percentage permeability and a residual resistance factor (RRF) were calculated. The sandpack represents sandstone reservoirs of fair porosity and permeability. After calculating pre and post gelation relative permeability of gel, RRF and PPR were calculated using following formula:

$$k = \frac{Q\mu L}{0.78 d^2 \Delta P} \qquad \text{..... (x)}$$

Where, Q is the flow rate (cm^3/s), μ, the viscosity of the brine (cP), L, the length of the sandpack holder (in cm), ΔP, the pressure drop (atm), d, diameter of sandpack (cm) and k, the permeability (Darcy).

$$RRF = \frac{\lambda_{wi}}{\lambda_{wa}} = \frac{K_{wi}\,\mu_{wa}}{K_{wa}\,\mu_{wi}} \qquad \text{..... (xi)}$$

$$PPR = 1 - \frac{K_{wa}}{K_{wi}} * 100 \qquad \text{..... (xii)}$$

Where, λ_{wi} and λ_{wa} are water mobility ratio before and after gel treatment, however, K_{wi} and K_{wa} are water absolute permeability before and after gel treatment.

7.2.2 Core Flooding Procedure

To test the effectiveness of the prepared gel system for water shut-off, a coreflood study was carried out using core**.** In this study, the Berea core was used**.** Berea core was placed in the stainless steel core holder**.** There were two outlets on the body of the core holder apart from inlet and outlet and all these four outlets on core holders were connected to the pressure transducers and pressure recording system for recording pressure at these points during flow studies. The core with core holder assembly was preheated in hot air to a desired temperature of 90ºC. A high-pressure syringe pump was used for pumping fluids in the core holder. The injection rate of the brine solution was 10 mL/hr. 3-4 Pore volumes of brine (2.0 % NaCl) and kerosene were passed through the core. Kerosene was also used as a pushing fluid for brine. Initially, the pressure was constant when the syringe pump was started. Darcy's permeability equation was used to calculate the value of pre and post gelation relative permeability to brine. Subsequently, after the brine and kerosene saturation, the gelant solution was injected in the core in a similar condition. Approximately 3-4 pore volumes of gelant was used to completely saturate the core.

A gelant sample from the same lot as used in the coreflood experiment was also kept separately in the same oven so as to ensure the formation of the gel inside the core. After the confirmation of gel formation, again brine and kerosene were injected through it at the same condition to find out the post gelation permeability to brine (Kumar et al., 2019; Singh and Mahto, 2015). The effluent of the brine sample was collected in a measuring cylinder with time and the relative permeability was calculated using the Darcy's equation.

$$K = \frac{Q\mu L}{A\Delta P} \qquad \text{..... (xiii)}$$

Where, k *is* permeability (Darcy), Q, the flow rate (mL/s), µ, viscosity of the fluid (cP), L, the length of core (cm), A, the cross-section area of the core (cm^2) and ∆P is the pressure drop across core (atm). After calculating pre and post gelation permeability of gel, RRF and PPR were also calculated using given below formulae.

$$\text{RRF} = \frac{\text{permeability to oil and water before gel injection}}{\text{permeability to oil and water after gel injection}} \qquad \text{..... (xiv)}$$

$$\text{PPR} = 1 - \frac{\text{post gelation permeability}}{\text{Pre gelation per meability}} * 100 \qquad \text{..... (xv)}$$

7.2.3 Calculation of the Diameter of the Core and Particles Before and After Gel Treatment

Ergun equation and modified Ergun equation was used to calculate particle diameter within the core. All required parameters of core and fluid properties were calculated during coreflood study.

7.3 Result and Discussion

7.3.1 Gelation Performance Study of PVP:RF, PVP/PVA:RF and PVA:RF Gels after Flowing Through Porous Media

Sandpack experiments were used to study the water shut-off capacity of the PVP, PVA based gel systems. The result indicated that the PVP:RF, PVP/PVA:RF and PVA:RF gel systems have good effectiveness in porous media. Furthermore, the stronger the gel strength, the higher the effectiveness in terms of PPR and RRF were observed. It can be seen for PVP:RF gel system in comparison to PVP/PVA:RF and PVA:RF gel systems. The experimental results have been shown in **Table 7.1.**

The gelant solutions were injected into the sandpacks. After 24 hours, more than predefined gelation time, gels were crosslinked and there was retention in the sandpacks. Through retention in the large channels, bridging across the pore throats and adsorption on the sand surface, these gels systems reduced the permeability into the sandpacks. Porosities of the sandpacks were found between 28-30%. It can be seen that the PPR and a residual resistance factor at 90ºC temperature are more than 90% and 14 respectively. All the gel samples have shown subsequent plugging effectiveness of the sandpack. PVA:RF gel system exhibits little low effectiveness than PVP/PVA:RF and PVP:RF systems. It may be due to the decrease in the crystalline properties of the PVA and salt effect. PVP/PVA:RF gel systems revealed moderate effectiveness, while PVP:RF system showed greater effectiveness than the former two gel systems. The gel system used in porous media showed the plugging ability and suitability of these gel systems for water shut-off treatments.

Table 7.1 Water shut-off capacity of gel systems by sandpack experiments

Gel systems	**Gel strength (Pa)**		**Relative permeability (md)**		**PPR**	**RRF**
	Fresh gel	**Effluent gel**	**Before**	**After**		
			Darcy	Darcy	(%)	
PVP:RF	26,000	22,500	0.594	.0271	95.44	21.88
PVP/PVA:RF	21,500	18,000	0.586	.0351	94.01	16.71
PVA:RF	18,000	15,000	0.575	.0410	92.86	14.01

The gel strength of fresh and effluent gel samples is shown in **Figure 7.2a.** Results show that PVP:RF gel system has higher gel strength in comparison to PVP/PVA:RF and PVA:RF gel systems. It can be seen in the depicted **Figure 7.2b** where residual resistance factor and percentage permeability reduction of blended polymer i.e., PVP/PVA:RF lies in between its parent’s polymer system i.e., PVA:RF and PVP:RF. PVA:RF has a lower viscosity. The crosslinking mechanism of gel in bottles for fresh gel samples and effluent gel samples (after sandpack floodings) and in porous media is depicted in **Figures 7.2 (c-e).** Original gel samples and effluent gel samples (PVP:RF, PVP/PVA:RF and PVA:RF) after sandpack flooding experiments were kept in a hot air oven at 90˚C temperature and aged for 24, 36 and 48 hours respectively.

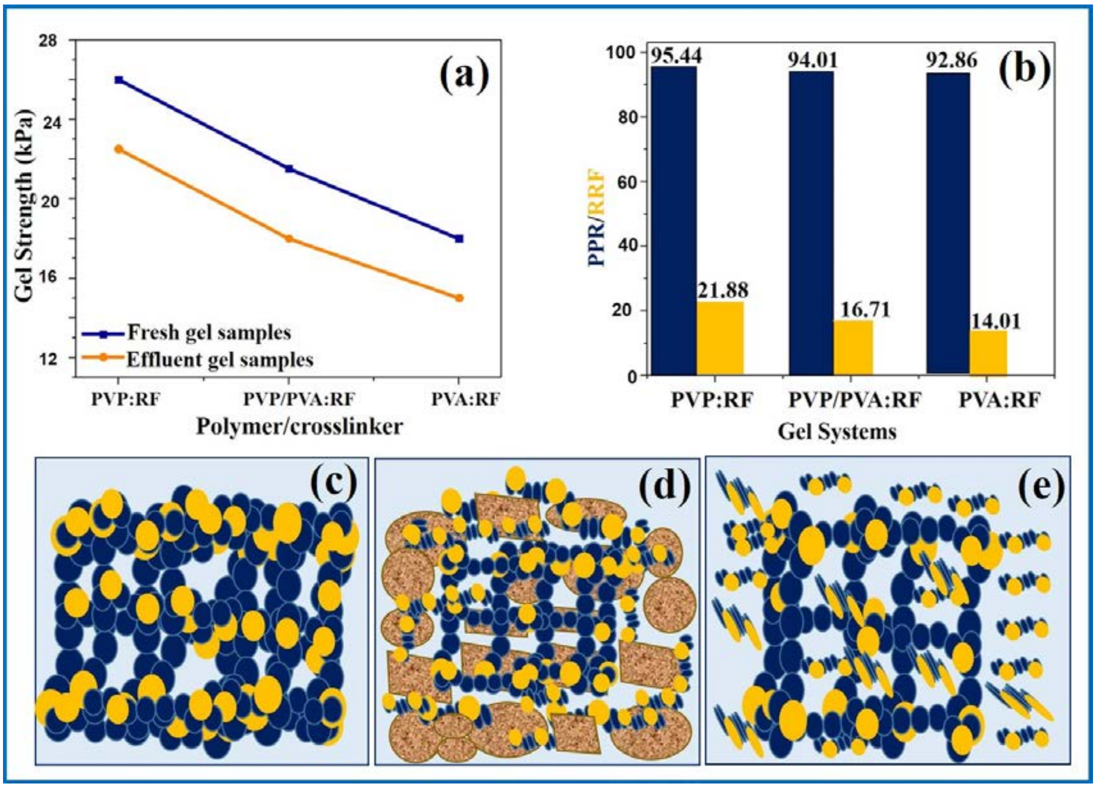

Figure 7.2 (a) Gel strengths of the fresh and effluent gel samples (b) Percentage permeability (c-e) Deformation of gel during sandpack flooding experiment.

Figure 7.3 Comparison diagrams of the gelation performance of the fresh and effluent (flowing through porous media) gel samples (a) PVP:RF (b) PVP/PVA:RF (c) PVA:RF.

In this study, the gelation performance of all three gel samples was continually observed through the bottle test to understand the difference of the gelation performance between the original gel samples and the samples after flowing through porous media. In **Figures 7.3 (a-c**) left bottles of gels show that the original gel samples have an obvious strong 3-Dimensional structure. For original gel samples, it is demonstrated that the preliminary net structure of gels is formed.

7.3.2 Sandpack Flooding Studies

For this experiment, the optimum solution of PVP:RF and PVP-ZnO:RF (polymer/ crosslinker ratio 1/0.25) was prepared. The porosity of the sandpack was found to be 28.30%. The experimental data of the sandpack study are shown in the **Table 7.2.**

Table 7.2 Sandpack study results for PVP:RF and PVP-ZnO:RF (5000 ppm)

Sl. No.	**Parameters**	**Observed values for gel systems**	
		PVP:RF	**PVP-ZnO:RF with 5000 ppm ZnO**
1.	Initial permeability before gel injection (Darcy)	3.8245	4.2602
2.	Post gelation permeability after gel injection (Darcy)	0.3009	0.1255
3.	Percentage permeability reduction (PPR) (%)	92.1213	96.6256
4.	Residual resistant factor (RRF)	12.7096	31.3094

Initially, the sandpack holder was kept in the preheated hot air oven at a temperature of 90ºC. The initial absolute permeability for brine was found to be 3.8245 and 4.2602 Darcy for PVP:RF and PVP-ZnO:RF gel systems. After that, the gelant solution was injected into the sandpack and it was kept in an oven at 90ºC for 3 days to ensure gelation. The schematic of the water shut-off mechanism is shown in **Figure 7.4.**

After gelation, the absolute permeability for brine was measured as 0.3009 and 0.1255 Darcy for PVP:RF and PVP-ZnO:RF gel systems. Percentage permeability reduction was 96.6256% and 92.1213% and residual resistance factor were 31.3094 and 12.7096 respectively for nanocomposite and conventional gels. It is shown in **Figure 7.5.** The result of both gel systems shows that the nanocomposite gel system showed more effectiveness than the conventional gel system into the reservoirs up to 90ºC.

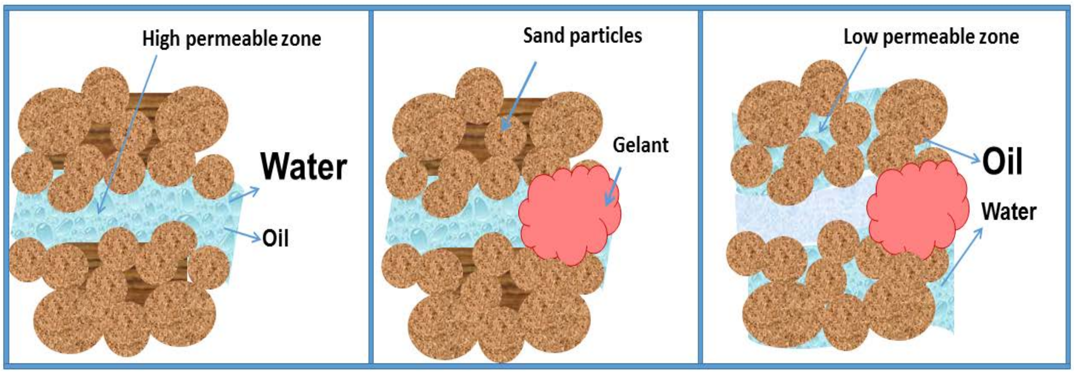

Figure 7.4 Schematic of produced water and management of excessive water (a) High permeable zone (b) Gel treatment in production well (c) Diversion of water in low permeable zones.

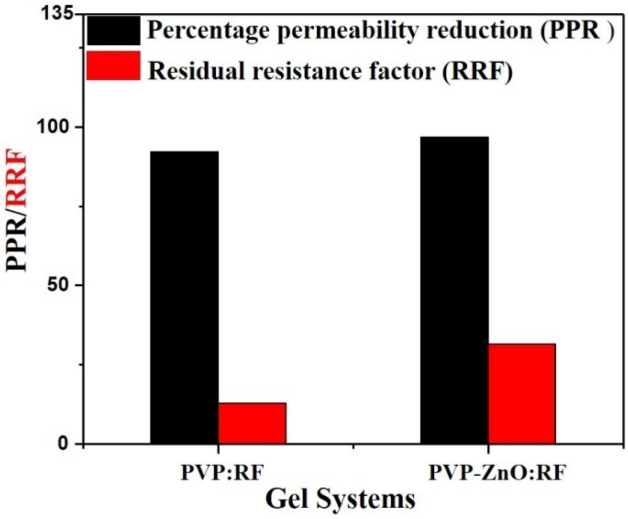

Figure 7.5 Percentage permeability reduction and residual resistance factor results of PVP:RF and PVP-ZnO:RF.

7.3.3 Coreflood Studies

For this experiment, the optimum solution of PVA:RF crosslinked gelant (polymer/crosslinker ratio 1/0.5) was prepared. The experimental data of the sandpack study is shown in **Table 7.3.** The initial relative permeability of brine was found to be 0.0025 Darcy. After that, the gelant solution was injected into the Berea core and the gelant containing core was kept in the preheated hot air oven for 3 days. After in-situ gelation, 2.0% NaCl solution (brine) was injected again into the core at 90˚C temperature to determine the effectiveness of the gel system. After gelation, the permeability of brine measured as 0.0001 Darcy. Percentage permeability reduction was 96% and the calculated residual resistance factor was found to be 25. The result showed that PVA:RF gel system can be effectively used in reservoirs up to a high temperature of 90ºC.

Table 7.3 Berea core data and experimental investigation results of the core flooding study

Parameters	**Results**
Core specifications	
Sample	Berea core
Length (cm)	3.834
Diameter (cm)	7.108
The dry weight of the core (gm)	191.551
Pore volume (cc)	11.5
Porosity	14.06%
Water recovered by displacing with (cc) oil	8
Initial oil saturation (S_{oi})	69.46%
Initial water saturation (S_{wi})	30.54%
Oil recovered by water flooding (cc)	6
% recovery of oil	75%
Residual oil saturation	17.36%
Pre relative permeability to brine (Darcy)	0.0025
Post relative permeability to brine (Darcy)	0.0001
Residual resistance factor for brine (RRF)	25
Percentage permeability reduction (PPR)	96%

7.3.4 Particle Diameter Calculation of the Core Using the Ergun Equation Before and After Gel Treatment

Using this equation diameter of core particles (D_p) before gel injection and increment in particle diameter (ΔD_p) after gel injection of the core can be calculated for Berea core. Pressure drop, before and after gel injection, flow rate and porosity of core were calculated during the core flood experiment (Ozahi et al., 2008). Core parameters, fluid properties, the diameter of core particles and change in diameter of core particles are given in **Table 7.4.**

Table 7.4 Core parameters and fluid properties

Core specifications and fluid properties	
Sample	Berea core
Length (mm)	71.08
Diameter (mm)	38.34
Flow rate (mL/min)	0.00277
void space or porosity (ϵ)	14.06%
Viscosity of 2% NaCl (μ) (Pa.s)	0.001036
Density of 2% NaCl (ρ) (g/mm^3)	0.001011
Initial pressure (ΔP_i) (Pa)	45000
Final pressure (ΔP_f) (Pa)	345000
particle diameter before gel injection (D_p) (mm)	39.84×10^{-5}
Particle diameter after gel injection (ΔD_p) (mm)	4.26×10^{-5}

Particle sphericity (Φ) was assumed 1 in this equation. The well-known equation was developed by Ergun, which is as follows:

$$\frac{\Delta P_i}{L}\frac{D_p}{\rho V_s^2}\frac{(\epsilon^3)}{(1-\epsilon)} = 150\frac{(1-\epsilon)\mu}{\rho V_s D_p} + 1.75 \qquad \text{..... (xvi)}$$

$$V_{s=}\frac{Flow\ rate}{\Pi r^2} \qquad \text{..... (xvii)}$$

where, ΔP_i (Pascal) is the pressure drop, which was calculated during the coreflood experiment as a function of brine flow rate (flow rate was 10 mL/s), $V_{s,}$ the flow velocity of brine at core surface (mm/s), L, the length of core (mm), ϵ, the void space or porosity of the core (dimensionless unit), ρ, density of brine (g/mm^3), μ, viscosity of brine (Pa.s) and D_p, particle diameter (mm).

After calculating the value of D_p, using eq. (xvi), modified Ergun equation was used to calculate ΔD_p.

$$\frac{\Delta P_f}{L}\frac{(D_p+\Delta D_p)}{\rho V_s^2}\frac{(\epsilon+\Delta\epsilon)^3}{1-\epsilon-\Delta\epsilon} = 150\,\frac{(1-\epsilon-\Delta\epsilon)\mu}{\rho V_s(D_p+\Delta D_p)}+1.75 \qquad \text{..... (xviii)}$$

Where, ΔP_f is pressure in Pa after gel treatment and $\Delta\epsilon$ is modified void space. $\Delta\epsilon$ can be calculated as below

$$\Delta\epsilon = \frac{P_m}{(P_{b-P_m})}\frac{3.\epsilon\;\Delta D_p}{D_p} \qquad \text{..... (xix)}$$

Where, P_b and P_m are bulk and medium densities (g/mm^3) of core particles respectively.

From the results, it can be concluded that particle diameter increases 10% after the gelation.

7.4 Conclusions

- All gel samples show good effectiveness in porous media.
- Remarkable permeability reduction was found in case of all the gels systems i.e., PVA:RF, PVP/PVP:RF and PVP:RF but PVP:RF gel systems which show highest- profile control performance.

- Compared with the result obtained from fresh and effluent gel sample, the gel strength of effluent obviously found to be decreased and the gelation time of effluent gel increased.
- The sandpack studies (at 75ºC temperature) revealed that the relative permeability of the sandpack decreased by 97% using nanocomposite gel as compared to conventional gel, which could reduce the relative permeability by 92%. Therefore, it can be concluded that PVP-ZnO:RF is more effective than PVP:RF.
- In PVA:RF gel system, core flood study was carried out to test effectiveness of gel system. The study showed impressive results of permeability reduction and residual resistance factor with no observance of infectivity problem. The gel system was thermally stable over a long period of time.
- Particle diameter increases 10% after the gelation.

CHAPTER 8

CONCLUSIONS AND FUTURE WORK

CHAPTER 8

CONCLUSIONS AND FUTURE WORK

8.1 Summary and Conclusions

To overcome excessive water problem and heterogeneity, the chemical methods including injection gelling systems, preformed particle gels, in-situ gels, foams, etc. have been widely used for excessive water control in oilfields globally. In recent decades, excessive water control or profile control was purposed to improve the efficiency of unwept zones, which has shown a clear effect on oil recovery. Among them, gels prepared by polymers crosslinked with crosslinkers have been demonstrated to be a cost-effective technique and usually applied for enhancing oil recovery factors by controlling excessive water. Even though soft materials are widely used in reservoirs, they need some enhancement in their gel strength, thermal stability and elastic properties under harsh reservoir conditions. While developing a new polymer hydrogel system for harsh reservoirs, some environmental conditions such as pH level, salinity and temperature are important to consider. In this research work we have synthesized hydrogels, blends gels and nanocomposite gels. Gelation study, thermal study, rheological study and in-situ gelation study of these gels was thoroughly studied.

The following conclusions were drawn from the present research work.

1. All the gel systems were prepared and screened for water shut-off treatment using bulk gelation studies and sandpack flooding experiments. During the gelation study of prepared gels, it was observed that on increasing polymer or crosslinker concentration, gel strength increased and gelation time

decreased. The temperature and salt effect was also checked of prepared gel systems. It was observed that at higher temperature gel strength increased and gelation time decreased and it was found that on increasing salt concentration gel strength decreased.

2. Fourier transform infrared spectroscopy (FTIR) analysis manifested the conclusion about the specific hydrogen bonding interaction between polymer and crosslinker and the results showed that due to hydrogen bonding, the frequency of –OH stretching mode decreased. Nanocomposite gel (PVP-ZnO:RF) showed a metal-oxygen bond that was absent in the conventional gel system (PVP:RF).
3. Field emission scanning electron microscopy (FESEM) results revealed the formation of 3D molecular structures in all gel systems. In PVA:RF gel systems it was observed that higher hydrogen bonding leads to the rough surface. Three-dimensional structure of PVP/PVA:RF gels showed a network structure in comparison to PVP:RF and PVA:RF gel systems.
4. Thermal studied was carried out using differential scanning calorimetry (DSC). This data confirmed the thermal stability of all three gel systems but PVP:RF gel system revealed higher thermal stability due to the presence of less bound water than PVP/PVA:RF and PVA:RF gel system. Thermal gravimetric analysis (TGA) analysis showed better thermal stability of nanocomposite gels (PVP:RF with ZnO) in comparison to conventional gel (PVP:RF).
5. Shear thinning and viscoelastic behavior of gels were confirmed by using a rheometer. Viscosities of gel systems were determined as a function of shear

rate and results demonstrated shear thinning behaviour of gels. At a fixed frequency, the complex viscosity increased for PVP:RF system. In PVA:RF gel systems, higher crosslinker concentration and nanocomposite gels (PVP-ZnO:RF) showed higher viscosity of gel. In all gel samples, the storage or elastic modulus(G') and loss and viscous modulus (G") were determined as a function of frequency and the result illustrated that elastic modulus is higher than the viscous modulus. It indicates the viscoelastic nature of gel systems.

6. Remarkable permeability reduction was found in the case of all the gels systems i.e., PVA:RF, PVP/PVA:RF and PVP:RF but PVP:RF gel systems which show highest-profile control performance. Sandpack study result concluded that the nanocomposite gel system shows more permeability reduction than the conventional gel system. Core flood experimental data of PVA:RF gel system confirmed the effectiveness of gel at 90ºC as the percentage permeability reduction result was 96%.
7. Using the Ergun equation it is confirmed that the diameter of core particles or particle size of Berea core increases almost 10% after gel injection. This result also confirms that PVA:RF gel system can be successfully used for water shut-off treatments at 90ºC.

8.2 Future Work

Although the provided results for hydrogels are quite good but some improvements can still be made. There are numerous lines of research arising from this work which should be pursued as well as identifying future topics to expand and further develop the reported research. The future recommendations and suggestions in the area of polymeric gels for water shut-off jobs in hydrocarbon reservoirs under reservoir conditions are the following.

- Firstly, the improvement in rheological (viscosity and elastic behaviour) and thermal (stability of polymers at high temperatures) properties of conventional and nanocomposite hydrogels.
- Secondly, the effect of different salt concentrations on hydrogels will be studied in detail to improve salt resistance capability of hydrogels.
- Finally, we would extend our core flood study of gels at different flow rates, pressure and salts.

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- **Reena**, Kumar, A., Mahto, V., Choubey, A.K., 2020. Synthesis and characterization of cross-linked hydrogels using polyvinyl alcohol and polyvinyl pyrrolidone and their blend for water shut-off treatments. J. Mole. Liq. 112472. https://doi.org/10.1016/j.molliq.2020.112472.
- **Reena**, Choubey, A.K. Polymers gels for water control in oil reservoirs: A review, Lap Lambert academic publication. https://www.morebooks.shop/store/gb/book/polymer-gels-for-water-control-in-oil-reservoirs:-a-review/isbn/978-613-8-84100-5.

Communicated

- **Reena**, Srivastava, V., Mahto, V., Choubey A.K. Experimental investigation of the gelation performance and sandpack study of laboratory synthesized ZnO reinforced PVP:RF gels for water shut-off treatment, Oil & Gas Science and Technology, 2021 (**Under review**).

Manuscript to be Submitted

- **Reena**, Choubey, A.K. Experimental investigation of the gelation performance of a novel polyvinyl alcohol-resorcinol-formaldehyde cross-linked gel system in porous media.
- **Reena**, Pandey, A., Choubey, A.K. Thermal and Rheological Investigations of a Polymer Nanocomposite SiO_2 based Gel System for Water Shutoff Applications.

Papers in International Conferences

- **Reena**, Choubey A.K., 2018. Gelation study of polymer gel for water control in petroleum reservoirs. Presented a paper in the “International Conference on Frontiers at the Chemistry Allied Sciences”, December 21st – 22nd 2018, Rajasthan University, Jaipur, Rajasthan.
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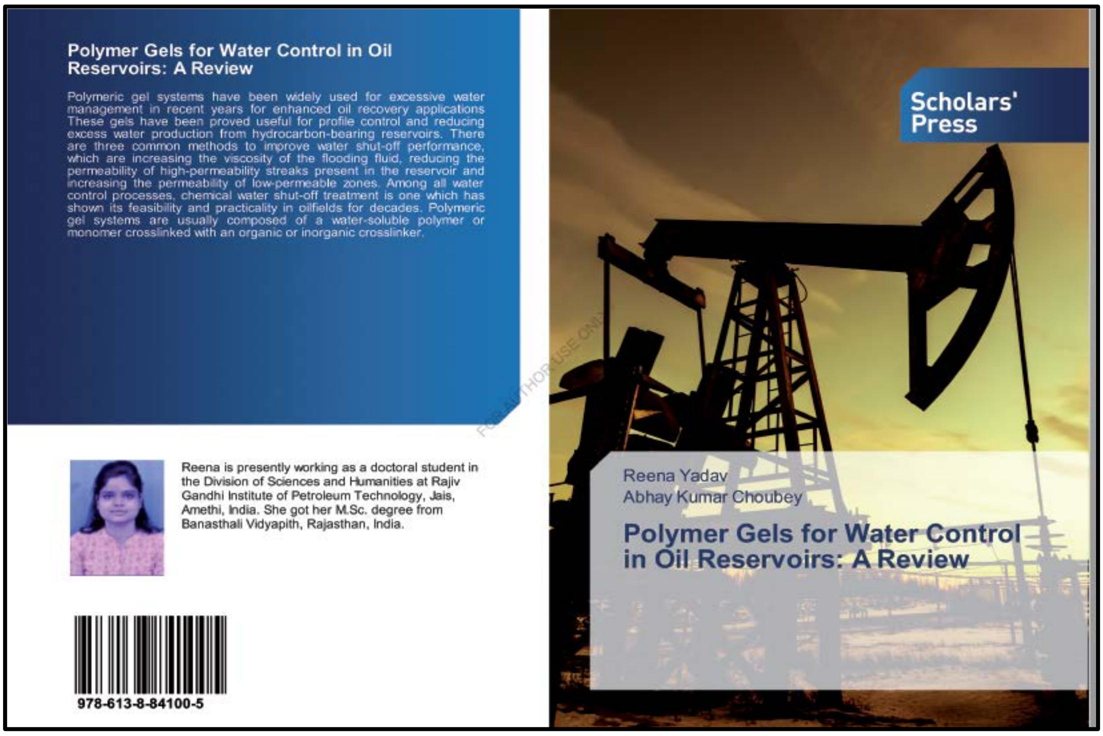

Polymer Gels for Water Control in Oil Reservoirs: A Review

Polymeric gel systems have been widely used for excessive water management in recent years for enhanced oil recovery applications These gels have been proved useful for profile control and reducing excess water production from hydrocarbon-bearing reservoirs. There are three common methods to improve water shut-off performance, which are increasing the viscosity of the flooding fluid, reducing the permeability of high-permeability streaks present in the reservoir and increasing the permeability of low-permeable zones. Among all water control processes, chemical water shut-off treatment is one which has shown its feasibility and practicality in oilfields for decades. Polymeric gel systems are usually composed of a water-soluble polymer or monomer crosslinked with an organic or inorganic crosslinker.

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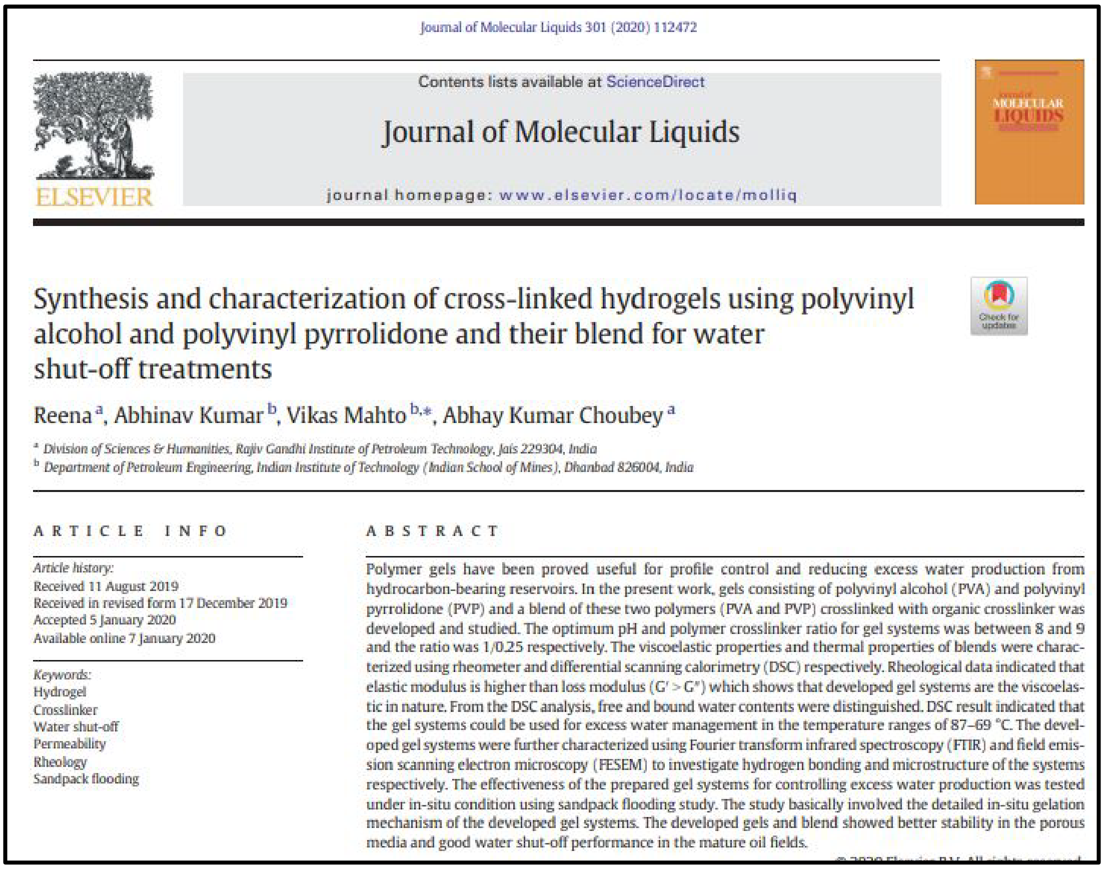
Polymer Gels for Water Control in Oil Reservoirs: A Review



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Synthesis and characterization of cross-linked hydrogels using polyvinyl alcohol and polyvinyl pyrrolidone and their blend for water shut-off treatments

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ABSTRACT

Polymer gels have been proved useful for profile control and reducing excess water production from hydrocarbon-bearing reservoirs. In the present work, gels consisting of polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) and a blend of these two polymers (PVA and PVP) crosslinked with organic crosslinker was developed and studied. The optimum pH and polymer crosslinker ratio for gel systems was between 8 and 9 and the ratio was 1/0.25 respectively. The viscoelastic properties and thermal properties of blends were characterized using rheometer and differential scanning calorimetry (DSC) respectively. Rheological data indicated that elastic modulus is higher than loss modulus ($G' > G''$) which shows that developed gel systems are the viscoelastic in nature. From the DSC analysis, free and bound water contents were distinguished. DSC result indicated that the gel systems could be used for excess water management in the temperature ranges of 87–69 °C. The developed gel systems were further characterized using Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM) to investigate hydrogen bonding and microstructure of the systems respectively. The effectiveness of the prepared gel systems for controlling excess water production was tested under in-situ condition using sandpack flooding study. The study basically involved the detailed in-situ gelation mechanism of the developed gel systems. The developed gels and blend showed better stability in the porous media and good water shut-off performance in the mature oil fields.